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Latex aggregation with methylcellulose

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LATEX AGGREGATION WITH METHYLCELLULOSE

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Abstract

Rheological measurements of polystyrene latex suspensions thickened with methylcellulose water-soluble polymer were performed with a cone-and-plate rheometer(Weissenberg rheogoniometer). Viscosity and normal forces of sheared suspensions were measured. Latex agglomeration was examined, and agglomerate sizes were measured by photon correlation spectroscopy, on a Coulter N-4 Nanosizer.

Polymer concentration was varied from .5% to 2.5%, with latex solids kept at 15% by weight. Latex had been previously cleaned of emulsifier or salt by the serum replacement cell technique, and the latex was thickened with three different molecular weight methylcelluloses (15,000 , 41,000 , and 86,000) .

Three zones of rheological behavior were observed. In the first zone, flocculation occurs as polymer concentration increases. This flocculation is attributed to depletion flocculation. Depletion flocculation is a result of particle interactions when a layer exists at the particle surface from which the polymer is excluded. In the second zone, increasing polymer concentration stabilizes the latex and increased latex stability reduces both viscosity and agglomeration. Increased stability is a consequence of depletion stabilization. In the third zone, viscosity increases with increasing polymer concentration, while agglomerate size does not change. This increase in viscosity is a result of polymer bridging and the increased solution viscosity.

The critical polymer concentration at the maximum depletion flocculation decreased as molecular weight increased. For the 4000 cp. and 400 cp. methylcellulose, the polymer concentration at maximum flocculation is .5%. For the 15 cp. methylcellulose, the polymer concentration at maximum flocculation is

1.2%.

The difference in viscosity between the flocculated and stabilized samples increased sharply with methylcellulose molecular weight. For high molecular weight polymer, at the critical flocculation concentration, phase separation between the latex and the suspending media occurs.

Chapter 1
Introduction

Rheological modification of latex paints is traditionally done with the help of cellulose derivatives, such as methylcellulose and hydroxyethylcellulose, and with alkali-swellable latexes. This work will show that the main effects of methylcellulose are to thicken the latex suspension by a bridging mechanism and by an osmotic force arising from the volume exclusion effect at latex surfaces, known as the depletion region effect. The depletion region effect coagulates the latex at a low polymer aqueous concentration, and at that concentration viscosity reaches a maximum.

The high latex viscosity at the depletion flocculation maximum is not observed during thickening of industrially produced latexes. Surfactants at the latex surface reverse the latex coagulation at the critical polymer concentration. Evidence for flocculation reversal has been provided in experiments subsequent to the work detailed below.

1.1 Rheology of Latex Suspensions

Several equations describe rheology of suspensions without polymer in the suspending media.

The rheology of latex suspensions without aggregation is described by modifications of the Einstein equation. The equation is

$$\eta_r = 1 + 2.5\phi \tag{1.1}$$

This equation is applicable to low volume fractions(ϕ<.01), and to non-interacting rigid spheres. It must be modified for deformable or interacting spheres, and for higher volume fractions(ϕ>.01).

Suspensions with high volume fractions (ϕ>0.2) show non-Newtonian behavior. Krieger [12] developed a model to describe the non-Newtonian flow of non-interacting rigid spheres through the crowding effect. The crowding effect takes place at high volume fractions (ϕ>.2).

Saunders [17] studied the rheology of monodisperse polystyrene latexes. He showed that his experimental data could be fitted to an extended Einstein equation. The extended Einstein equation means more terms with volume fraction as a variable are present. An example is the following equation.

$$\eta_r = 1 + 2.5\phi + a\phi^2 \qquad (1.2)$$

The constant a is in the range from 5 to 14 [9], and it accounts for interaction between the particles due to simple crowding.

For systems without polymer, but with simple aggregation, Gillespie [9] proposed a modified Brinkman equation.

$$\eta_r = 1/(1-s\phi^{kE}) \qquad (1.3)$$

The Brinkman equation is an extended Einstein equation. The parameter s has been added in order to include the enclosed volume of the aggregate into the equation. This equation is applicable to non-deformable aggregates at high volume fraction.

The pseudo-plastic model for latex suspensions includes a Bingham yield stress, and a plastic viscosity. Both are found by extrapolating the linear portion of a stress vs. shear rate plot to the stress axis. The descriptive equation is as follows.

$$\tau = \tau_B + \eta_{PL}\gamma \qquad (1.4)$$

Firth and Hunter [6] presented a modified pseudo-plastic model to explain

rheology of salt-coagulated hard and deformable colloids (TiO_2,PMMA,silica). This model is called the elastic floc model, because the Bingham yield stress includes a parameter for the separation energy of two particles. The energy of interaction for two-particle flocculation can be used as a rheological parameter.

1.2 Rheology of Latex with Polymer in Solution

Published experiments with latex suspensions and polymer in solution have focused on systems with surfactant present. The present study has been performed with no surfactant, and only soluble uncharged polymer with a single monomer type has been used. Furthermore, salt has been added in many published experiments, while in the present work salt is not added.

Neville and Hunter [14] developed models for the viscosity of sterically stabilized latex in which the Van der Waals forces and the steric repulsive forces are included in the model. The behavior is assumed to be pseudo-plastic. The latex is stabilized with adsorbed non-ionic polymeric surfactant.

Saunders [15] studied the rheology of thickened latexes with the surface tension brought to a minimum by addition of emulsifier. Saunders used 15 cp. methyl cellulose and varied polymer concentration from 1.6% to 3%. Latex volume fraction was high (ϕ=.26). Viscosity hysteresis was observed. The pseudo-plastic rheological behavior was attributed to bridging and it was shown that by decreasing interparticle distance with smaller particles, bridging is increased. Increasing polymer concentration increases bridging and viscosity, but the size of the viscosity hysteresis after shearing is constant with changing polymer concentration.

Heath and Tadros [10] experimented with two water-soluble polymers present in the suspension. One polymer is a block copolymer which adsorbs to

the latex surface, and the thickening polymer is poly(ethylene oxide). NaCl is present at .01 M . Their results were similar to those of Saunders [15] ; the suspension viscosity was found to increase monotonically with poly(ethylene oxide) concentration.

Hunter, Matarese, and Napper [11] used a positively charged polymer to bridge negatively charged surface groups of the latex. Salt, .001 M KCl, is present, and a high molecular weight polymer is used ($5x10^6$). The latex is prepared without surfactant. Destabilization(flocculation) of latex occurs at a polymer concentration of .06%, and stabilization of latex occurs at a polymer concentration of .12%. Beyond a polymer concentration of .12% increasing polymer concentration increases viscosity. This result is similar to the result proposed by the model provided in this thesis.

1.3 Evidence for Depletion Flocculation and Stabilization

Gillespie [8] performed experiments at very low solids fractions (ϕ<.001%) to determine the effect of soluble polymer (methylcellulose) on latex stability. A high molecular weight methylcellulose was used (4000 cp., MW_n=86,000). Dilution lowered electrolyte concentration to $7.4x10^{-6}$ %, and surfactant to $2.8x10^{-5}$%. Latex diameter was .58 microns. A flocculation maximum was observed at .25% methylcellulose, and a stabilization was observed at .5% methylcellulose. This effect was referred to in the article as a sensitization-stabilization effect and may be an early observation of depletion region phenomena.

Saunders and Sanders observed [16] similar phenomena with a low molecular weight methylcellulose (15 cp.). The surface tension of these systems was 72 dynes/cm., which indicates a surfactant-free suspension. Polystyrene

latex concentration was low (.82%) and latex diameters at .13 and .3 microns were used. Electrolyte and emulsifier were added to vary the position of an observed flocculation maximum. As electrolyte increased in concentration, polymer concentration at flocculation maximum decreased. A stabilization effect was observed at higher polymer concentrations.

Sperry, Hopfenberg, and Thomas [20] used a latex with a particle diameter of .85 microns to measure how thickener molecular weight (hydroxyethylcellulose), emulsifier concentration, and electrolyte concentration effect the critical polymer concentration at the flocculation maximum. Initial electrolyte concentration was .01% of solution, and .001% surfactant is present in the solution. Latex solids fraction was 20% (ϕ=.2). The experiments with emulsifier and electrolyte concentration produced results similar to Saunders [16]. The experiments also show that a reduction in critical polymer concentration occurs when soluble polymer molecular weight increases.

Sperry [19] prepared samples for measurement with .2% nonionic emulsifier present, and .5% ionic emulsifier. No stabilization was observed, and flocculation occurred at very high hydroxyethylcellulose concentrations. Sperry proposes a osmotic pressure model similar to the original Oosawa model [1], with no provision for stabilization .

The above experiments have limited resemblance to the experimental work detailed in this thesis. Only Sperry et al. [20] used high volume fraction(ϕ>.05). However, none provided both emulsifier-free and salt-free samples. Stabilization points were provided only in Saunders et al. [16] and in Sperry et al. [20]. The aqueous experiments above did not document phase separation of latex coagulum, and this may be due to the presence of surfactant in most cases.

DeHek and Vrij [3, 4] examined the flocculation of non-aqueous suspensions by soluble polymer. Silica was dispersed with stearyl alcohol in a cyclohexane solution of polystyrene. The silica particles had radii ranging from 21 to 71 nanometers. Depletion flocculation by polystyrene was observed, and the reduction in the critical polymer concentration with increasing polystyrene molecular weight was also demonstrated. A model based on osmotic pressure and the surface exclusion of soluble polymer was used to explain the particle flocculation. Because of the high molecular weight of the polymer and the small size of the particles, phase separation was observed in almost all samples.

1.4 Models for Depletion Theory

Oosawa and Asakura [2] published the first description of depletion phenomena. This theory proposes that if the polymer in solution is considered as a hard sphere, it cannot enter a gap between two plates where the gap is smaller than the molecule diameter. This theory correlates polymer radius of gyration with the depth of the depletion or exclusion layer. Osmotic pressure on the outside of the plates forces the plates together.

In a subsequent article [1] they describe the forces between two spherical particles. They showed that the area over which the osmotic force acts is a circle with the diameter of the particles.

Feigin and Napper [5] described an attraction between particles based on the free energy of solvent mixing when the polymer-free solvent between particles is mixed with the continuous phase after the particles flocculate. This is analogous to the osmotic pressure explanation. Feigin and Napper provide a thermodynamic explanation for the energy barrier which results in kinetic stabilization of the latex.

Scheutjens and Fleer [18] proposed a lattice model for polymer segment density and surface excess between two plates. Surface excess is correlated to free energy changes on the approach of the plates. This theory predicts both depletion flocculation and stabilization. In a later article, Scheutjens, Fleer, and Vincent [7] rejected kinetic stabilization as an explanation for depletion stabilization.

None of the above models include a criteria for phase separation.

Chapter 2
Latex Aggregation with Water-Soluble Polymers

2.1 Osmotic Forces, and the Volume Exclusion Effect

The entropy of a polymer is lower at a latex surface, as shown by Scheutjens and Fleer [18] . Thermodynamic potential μ_i at the latex surface and in the solution must be equal. An osmotic pressure Π and a polymer segment density gradient appear at the latex surface as a consequence of equal thermodynamic potential μ_i at equilibrium. Polymer segment density at the latex surface is lower than in the solution. This lower segment density occurs in the depletion layer or exclusion volume, because the polymer is depleted or excluded at the latex surface.

Because of the significant exclusion volume of polymer molecules, the concentration of a polymer at the surface of a latex particle is different from the bulk polymer concentration .

A model is proposed here for the effect of methylcellulose concentration on aggregate size and dispersion viscosity based on the consequences of the exclusion volume effect. Figure 2-1 illustrates the rheological behavior of a thickened latex predicted by the model presented below. The rheology of thickened latex prepared by procedures outlined below follows this model behavior.

In Zone 1, agglomeration by polymer in solution is increasing. Polymer in solution results in depletion flocculation. Aggregate size and viscosity increase to a maximum. In Zone 2 polymer in solution results in the depletion

stabilization effect. The rheology and the aggregate size decrease to a minimum. In Zone 3 viscosity increases with concentration by a bridging mechanism which occurs at high surface coverage and by increased solution viscosity.

2.2 Aggregation by a Mixed Bridging-Osmotic Pressure Mechanism

The mixed bridging-osmotic pressure mechanism is intended to show that for all soluble polymers both bridging and the surface exclusion effect play significant roles in causing particle aggregation. Four steps are outlined below, which show how this process can occur for both charged polymers and for neutral polymers which bind to surface sites.

Step 1

Bridging by water-soluble polymers is the first step in flocculation. Bridging means that segments of the polymer in solution are adsorbed on two or more latex particles. This bridging polymer may be charged or uncharged. The role of bridging in particle flocculation is to keep the two particles near each other while depletion flocculation takes place.

An example of a flocculating charged polymer is a copolymer of vinyl pyridine and acrylamide. The vinyl pyridine has positively charged sites, which can bind to a sulfate group on a latex surface.

For a uncharged water-soluble polymer, bridging may occur by the binding of hydrophobic segments of the polymer to hydrophobic areas of the particle surface.

Step 2

When two particles first approach, there must be a force arising from the depletion attraction large enough to empty the interparticle volume. There is a balance between the two osmotic forces (the stabilizing force, and the attracting force) which results in aggregate size equilibrium . This is described in Section 2.3.

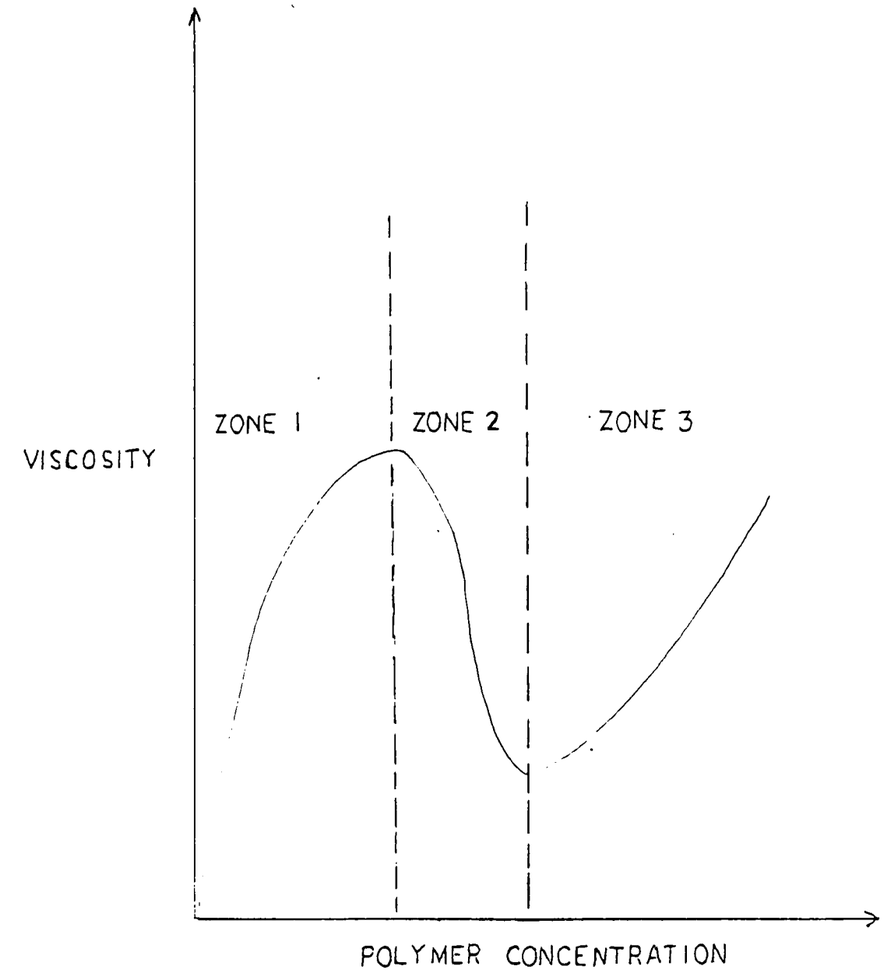

Figure 2-1: Three Zones of Rheological Behavior

The gap between the two particles must be free of polymer for flocculation to occur. Polymer must diffuse out of the interparticle volume before depletion flocculation takes place. The time of proximity of the two particles must be greater than the inter-particle volume-emptying time. The time the polymer bridge stays adsorbed to both particles controls the time the two particles are near to each other.

The theory of bridging states that bridging is improved with larger polymers. Improved bridging improves the equilibrium in favor of depletion flocculation.

For highly charged colloids, the bridging may also neutralize the charges on the surface, when the colloid surface and the polymer charged group have opposite signs. This can lead to a decrease of the electrostatic repulsion forces.

Step 3

The bridging polymer must diffuse out of the interparticle gap. This diffusion may occur more slowly than for unadsorbed polymer because the bridging polymer must desorb before diffusion.

Step 4

The particles come together when the Van der Waals attraction plus the osmotic force are greater than the electrostatic repulsion. This would take place when a larger osmotic force, associated with a larger depletion (exclusion volume) is present. This condition is met with high-molecular weight polymers, because exclusion volume depth is proportional to the polymer end-to-end distance.

2.3 Aggregate Size Equilibrium using Force Balances

The most recent debate concerning the nature of the depletion region, or volume exclusion effect, has been whether the flocculation produces an equilibrium agglomerate size or whether flocculation produces a phase-separation phenomena. Phase separation means collection of the colloids or latexes into one phase, and the sera into another phase [3].

A related question is whether depletion flocculation produces metastable states. A metastable state is a state where the agglomerate is stable with time but is not at equilibrium size. This question has been debated in the articles of Vincent, Scheutjens, and Fleer [18, 7].The agglomerate can reach the equilibrium size by a shearing process, which provides energy to surmount the energy barrier between the metastable and the equilibrium state. This description is also called the kinetic description of depletion flocculation. The kinetic description uses a particle pair potential with a potential well and an energy barrier. This kinetic description is supported by the large viscosity hysteresis appearing in thickened latex viscosity measurements in Zone 2 shown in Figures 4-8 to 4-12.

The agglomerate size equilibrium involves a balance of two forces. The first force is the resistance to diffusion by the polymer out of the volume between two particles or agglomerates (which is resistance to osmotic pressure). The second force is the osmotic pressure at the boundary of the exclusion volume at the particle surface. This second (flocculation) force takes place over the particle cross-section area (πr^2), where r is particle radius.

2.4 Model for Flocculation

The model diagram for the depletion stabilization model is shown in Figure 4-2. Consider two particles of radius r. The bulk polymer concentration is C_0. Osmotic pressure at any depletion layer surface is $\Pi(C_0)$. The cross-sectional area over which the osmotic forces are present has a differential element dA and a total area πr^2.

X is the total distance between particle surfaces for any differential element. At any X, as the particles approach, there is a segment density function of x, along the distance X. C(x) is defined by C(0)=0, C(X)=0, and dC(X/2)/dx=0. This means C is maximum at the dividing plane between the particles, and 0 at the particle surfaces. Define C_{avg} as an average of C over X.

Treat each osmotic pressure on dA, where a differential volume of solution and a differential amount of polymer is removed from the interparticle volume as the particles approach. This differential volume is dAdX, and dX is the change in the interparticle distance X when the particles are approaching one another.

The change in the amount of polymer between the particles in dA is $d(dAC_{avg}X)$, or

$dA(dC_{avg}X+dXC_{avg})$

The concentration of polymer in the removed differential volume is $XdC_{avg}/dX+C_{avg}$.

This quantity is called C_Δ.

To obtain the total force, integrate using θ as the angle from the interparticle axis, and integrate, at separation d_0 along the main axis, between $\theta=0$ and $\theta=\pi/2$.

For any θ, $X=d_0 + 2r(1-\cos\theta)$.

Force in a differential annular area is $|\Pi(C_0)-\Pi(C_\Delta)|dA$.

The differential annular area is $dA=2\pi r \sin\theta d(r\sin\theta)$.

$$F(total)= \{_0^{\pi/2} 2\pi r \sin\theta|\Pi(C_0) - \Pi(C_\Delta)| d(r\sin\theta) \quad (2.1)$$

Define two areas. The area where $\Pi(C_0) - \Pi(C_\Delta)>0$ is within the circle $\theta<\theta_1$. The area where $\Pi(C_0) - \Pi(C_\Delta)<0$ is in the annulus defined by $\theta_2>\theta>\theta_1$. As R (agglomerate radius) increases, F(total) decreases as the size of the outside annulus increases, and a point is reached where stabilization at larger agglomerate sizes results.

When the agglomerate diameter is larger, the flocculation force is smaller. An equilibrium size is reached when F(total)<0. Phase separation occurs when the flocculation force is much larger than the stabilizing force. At phase separation, for all separations F(total)>0, even at very large agglomerate diameters.

An alternate model, presented by Feigin and Napper [5], considers the change in the free energy when the particles collide. ΔG is equal to the free energy change when mixing the solvent in the particle inter-volume is mixed with the continuous phase. When $\Delta G<0$, agglomeration occurs.

In certain cases, the aggregate size is determined by the way the sample is prepared. The mixing process can lead to aggregates in a metastable state which will be destabilized with shearing.

The two variables, solids volume fraction, and polymer concentration, define two regions. Agglomerate size is defined in a region in Zone 1 and Zone 2 where the molecular weight is low($MW<10^4$) and the particle size is large(r>75 nanometers). Phase separation occurs near the flocculation maximum

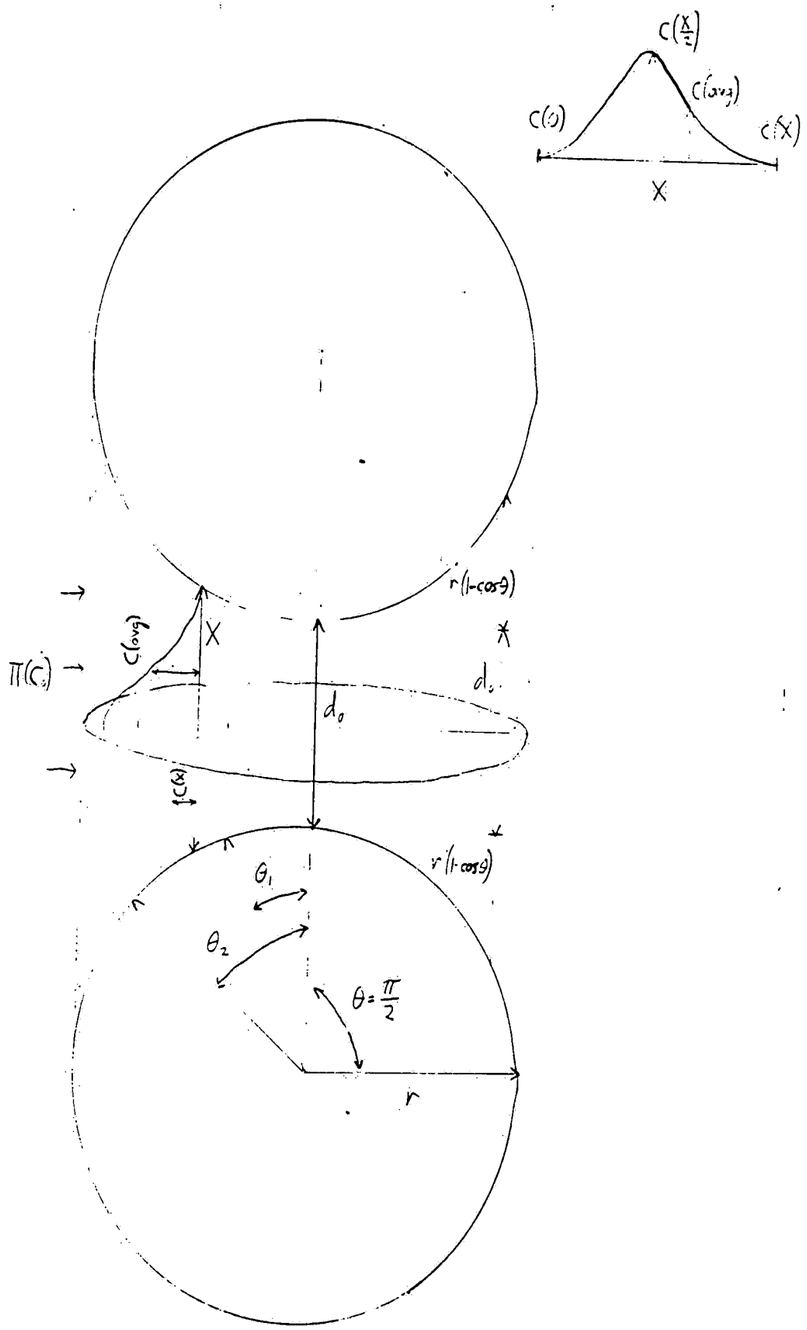

Figure 2-2: Model for Agglomerate Size Equilibrium

polymer concentration, for high molecular weight polymer($>10^5$) and small (r<75 nanometers) . The above model shows that agglomerate size and the point of phase separation depends on a balance of stabilizing and flocculating forces between the two particles during their approach. Equilibrium agglomerate size can be predicted by treating two agglomerates as two particles approaching one another.

It is essential that any theory of depletion flocculation include several features.

(1) A description of how both depletion flocculation and depletion stabilization occur.

(2) A model for agreggate size equilibrium.

(3) A model for the conditions under which phase separation takes place.

The model proposed above meets these criterion. A description is provided of both stabilization and destabilization criteria. In addition, the point at which phase separation occurs is identified. Further, the equilibrium agglomerate sizes can be predicted by the above model if the segment density distribution functions are provided. The details not provided above are the polymer segment density distribution functions for two particles as they approach one another.

The models of Feigin and Napper [5], and the original model of Scheutjen and Fleer [18] do not provide a prediction of when phase separation whether takes place. The models of Sperry and of Vrij do not provide a description of depletion stabilization.

Chapter 3
Experimental Methods

Thickened polystyrene latexes are prepared having a particle weight fraction of ϕ=.15. Methylcellulose concentration (based on the weight of aqueous phase) is varied from .25% to 3%. Three methylcellulose molecular weights are used.

The methylcellulose is provided by Sigma Chem Co.. The molecular weights(number average) are 15,000 , 41,000 , and 86,000, and were provided by the original supplier to Sigma Chem. The three standards are referred to as 15 cp.,400 cp., and 4000 cp.

Samples are sheared in a Weissenberg cone-and-plate rheogoniometer. Viscosity and normal force are measured. Agglomerate size is measured by photon correlation spectroscopy using an N-4 Coulter Electronic Nanosizer.

3.1 Sample Preparation

The methylcellulose in powder form is mixed with distilled, deionized water. The 50 ml. bottles are shaken by hand, and then .25-.5 ml. of 1.1% sodium azide solution is added to each bottle. The bottles are then stored in a refrigerator for two days before use, because methylcellulose increases in solubility as temperature is reduced from room temperature. The sodium azide is a bactericide, used at .55 to 1.1×10^{-4} weight fraction, or $.72\text{-}1.45 \times 10^{-6}$ moles/ltr(1.45×10^{-3} millimoles/liter).

The latex is monodisperse polystyrene, with a diameter of .19 microns. The latex has been cleaned in a serum-replacement cell until the eluant of the cell has a conductivity equal to the DDI water used for cleaning. This low-solids

cleaned-latex suspension is concentrated in a Roto-Vap evaporator.

The methylcellulose solution is added to the latex sample and the mixture is mixed by hand for 20 seconds using a steel spatula. The sample is then set aside to equilibrate for 2 hours before testing.

The final concentration of methylcellulose in the aqueous phase will vary between .5% and 3%. Our main interest is to observe the changes in thickened latex rheology with changes in methylcellulose concentration.

3.2 Viscosity Measurement Using the Weissenberg Rheometer

All samples were measured using a Weissenberg Rheogoniometer, which is a cone and plate viscometer. The cone angle was 1 degree, and the platen diameter is 5 cm. The experiments were performed at room temperature, typically at 20.5 C. Viscosity is calculated as the ratio of the measured value of shear stress on the cone to the applied shear rate.

For the measurement of viscosity near the depletion flocculation maximum, care must be taken during sample placement on the plate. The presence of large agglomerates can prevent the rheometer from measuring with good accuracy. This is possible when a cake or mass of coagulated latex attaches to the plate or cone. The attached coagulum may decrease the gap between plate and cone, and consequently increase the applied shear rate. This may result in inaccurate viscosity data. If the cone and plate gap varies because of attached macroscopic agglomerates, differences in local shear rate may appear. This may lead to erroneous viscosity measurements, since the cone-and-plate rheometer calculations are based on a single shear rate at all points under the cone.

Shearing in this region can lead to further agglomeration, and to phase separation. Phase separation is discussed in the experimental sections.

Hysteresis appears when shear rate is raised and then lowered. The viscosity is smaller when the shear rate is lowered than when the shear rate is raised. This is shown in Figures 4-10 to 4-14 where viscosity hysteresis is shown decreasing in magnitude as polymer concentration increases.

3.3 Normal Force Measurement

Normal force measurement is performed on the rheometer mentioned above. The displacement of a spring attached to one of the shearing surfaces provides the magnitude of the first normal force. This normal force provides information on the elastic properties of the sample. A positive normal force indicates the presence of elastic properties in the sample measured. At high shear rates, the centrifugal forces may force fluid out from the plates and produce a false negative normal force. This fact should be taken into account when calculating true normal forces at high shear rates. A correction for centrifugal force must be added to measured normal force at each high shear rate.

The compression of a sample when the cone is brought down onto the plate may compress large agglomerates onto the plate. This occurs near the depletion flocculation maximum where agglomerates are macroscopic. An over-measurement of normal forces may result. In some cases where the agglomerates are macroscopic a normal force appears when the sample is not sheared, but the cause of this is not known.

3.4 Aggregate Size Measurement

Each sample had its agglomerate size measured using the N-4 Coulter Counter. The N-4 is an automated particle size measuring device which uses photon-correlation spectroscopy. Photon-correlation spectroscopy(PCS) measures the phase shift of light from a laser after scattering by suspended particles. The computer treats the combined waveform for all particles using an Auto-Correlation Function, and a scattering intensity can be allocated to each Doppler phase-shift. This intensity is equivalent to the number of particles with that phase shift times the cross-sectional scattering area of that particle. The particle diameter is calculated based on Stokes-Einstein equation and a diffusion constant known from the Doppler shift and the Auto-Correlation function. The range of accurate measurement for the N-4 Coulter Counter is between 100 and 10,000 nanometers.

We then obtain the particle size distribution, and a cumulant diameter average based on light scattering intensity. The cumulant average weights the average based on particle cross-sectional area. Nine measurements are made, and then averaged to obtain the data shown in Figures 4 and 5.

Samples thickened with 400 cp. and 4000 cp. methylcellulose were measured for agglomerate size after shearing. This was done so that the sizes would better reflect the equilibrium size. It is hypothesized the agglomerate is closer to the equilibrium size after shearing. The latex thickened with 15 cp. methylcellulose was not measured after shearing because sheared samples had not been saved.

Samples for measurement are prepared by dilution of a latex sample in distilled deionized water. If an agglomerate is unstable with dilution, it will not

be measurable with this method. The agglomerates produced by bridging are believed unstable on dilution. But agglomerates produced by depletion flocculation or salt-induced coagulation have the particles in direct contact. Particles in direct contact are in an energy well because of a negative enthalpy change on coagulation. Agglomerates in this energy well are believed to be stable up to 24 hours after dilution. No reference is available for stability on dilution, and an experiment should be performed to verify the above assertion.

Particle size distribution data are not included in this thesis because of the lack of reproducibility of the distributions produced by the Nanosizer computer. Several runs produce several different distributions for a single sample. For example, the 2% polymer sample using 400 cp. methylcellulose to thickener latex was measured nine times for average agglomerate size and particle size distribution. The same sample produces two trimodal(three peak) distributions , and one bimodal distribution. The extraction of the distribution from the scattering data is not reproducible for a single sample. In addition, the program which calculates the distribution cannot describe distributions for particles greater than 10,000 nanometers in diameter. These are identified as dust, and the quantity of dust varies for each distribution result(for the same sample.)

Chapter 4
Results and Discussion

4.1 15 cp. Methylcellulose

The methylcellulose with the lowest molecular weight had a number average molecular weight of 15,000. The viscosity in a 2% solution is 15 centipoise, and this methylcellulose sample is referred to hereafter as 15 cp. methylcellulose. Rheology data for polymer solutions is displayed in Figure 4-1 and 4-2 for 1.5% and 2% polymer in water. We prepared latex mixtures with methylcellulose where the concentrations are .5%,.75%,1.2%,1.5%,2%, and 3%.

Rheology

Viscosity measurements at a shear rate of 22.12 sec^{-1} are shown in Figure 4-3. Low shear rate data is displayed for comparison with the data from high molecular weight methylcellulose-thickened latex. The viscosity measurements were made in all three zones. Thickened latex viscosity increased in Zone 1, decreased in Zone 2, and increased again in Zone 3. A plot of relative viscosity versus polymer concentration for 15 cp. methylcellulose is provided in Figure 4-4 for viscosity at shear rate of 22.12 sec^{-1}.

Yield Stress and Plastic Viscosity

Shear stress is obtained from rheometer data for the thickened latex. Yield stress (τ_B) and plastic viscosity (η_{PL}) were obtained for latex thickened with 15 cp. methylcellulose . This data is found assuming the pseudoplastic model.

$$\tau = \tau_B + \eta_{PL}\gamma$$

The yield stress is obtained by extrapolating shear stress to zero shear rate, on a plot of shear rate versus shear stress.

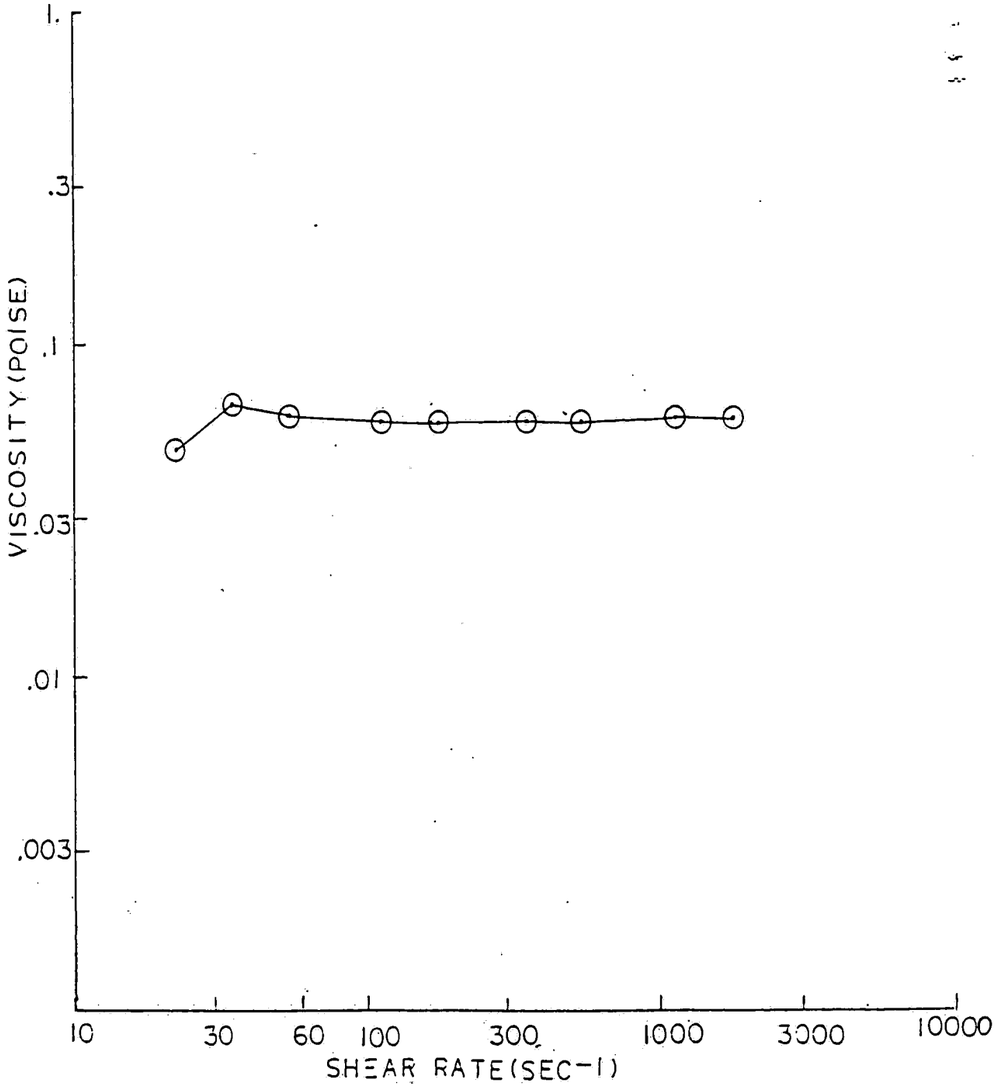

Figure 4-1: Viscosity of 1.5% 15 cp. Methylcellulose

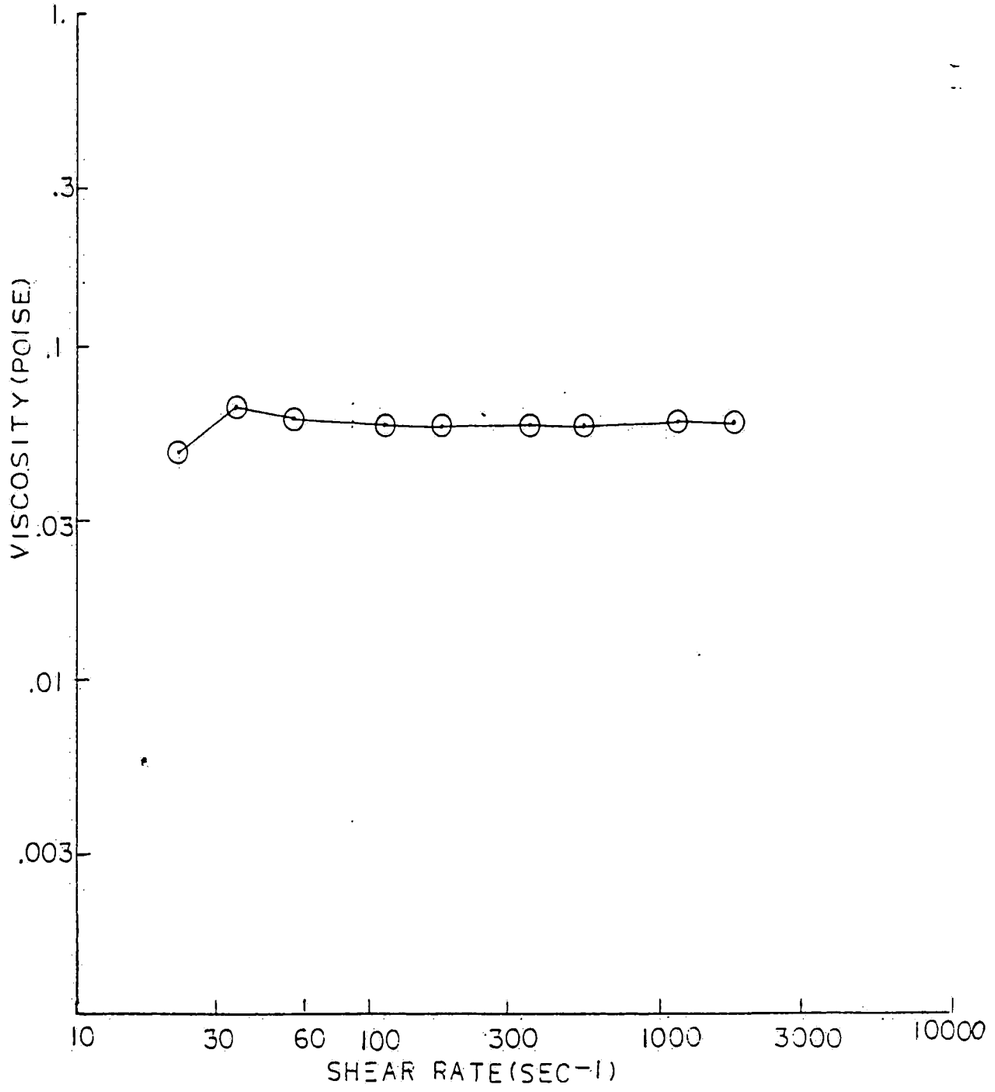

Figure 4-2: Viscosity of 2% 15 cp. Methylcellulose

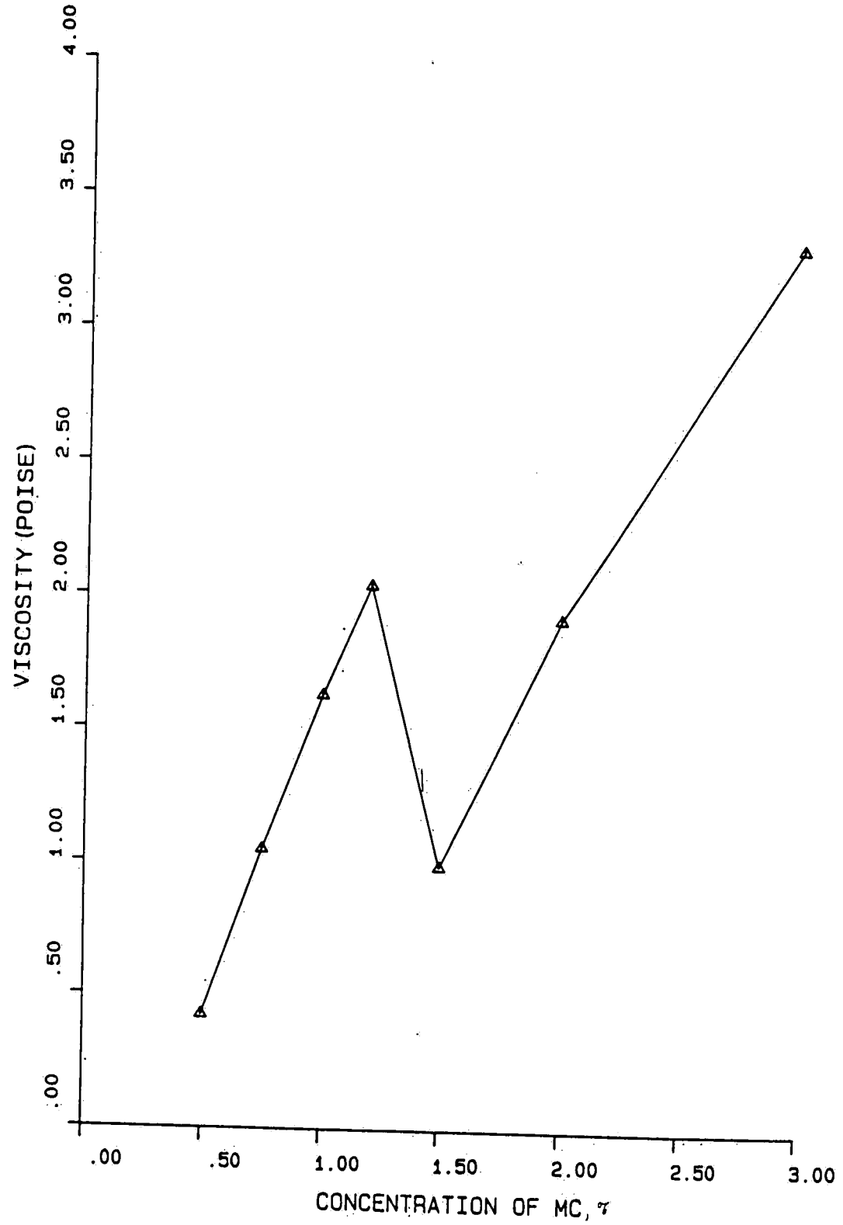

Figure 4-3: Rheology of Latex with 15 cp. Methylcellulose

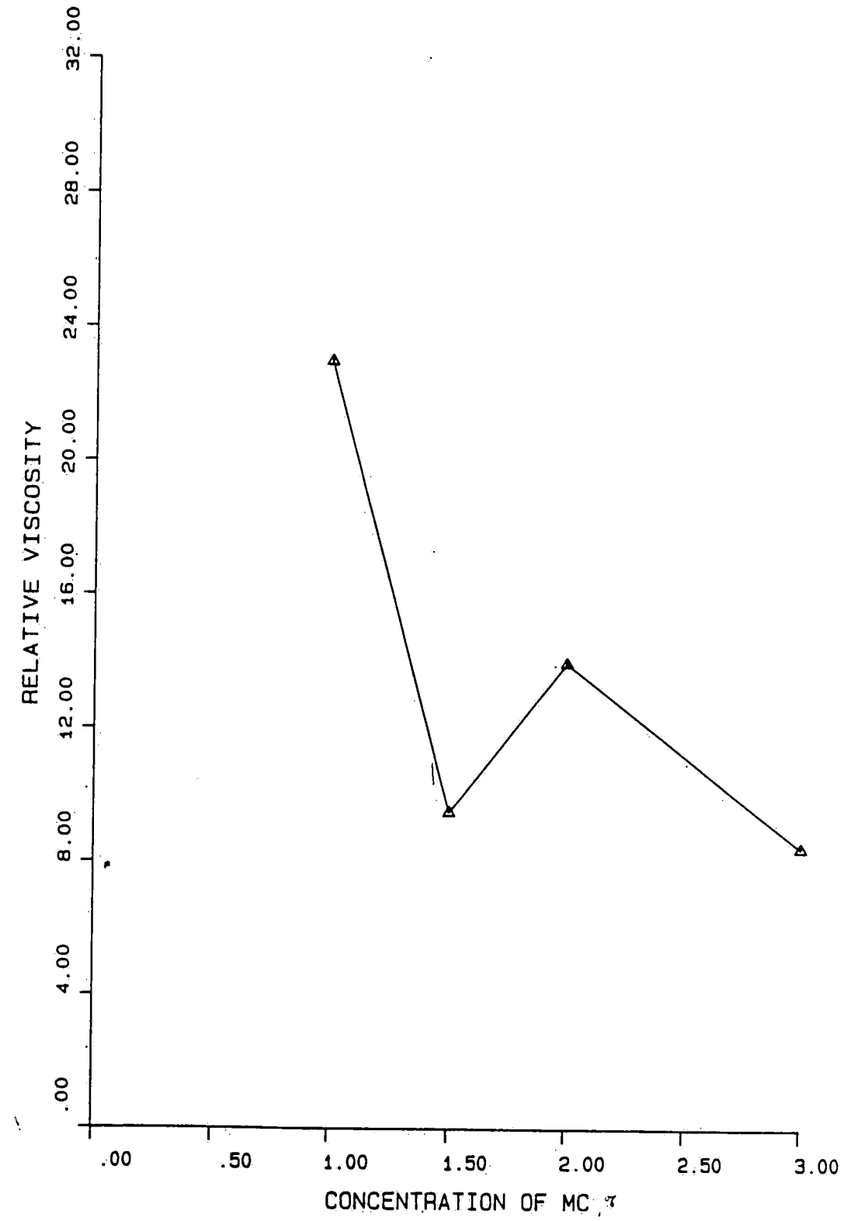

Figure 4-4: Relative Viscosity of Latex with 15 cp. Methylcellulose

Data for yield stress is shown in Table 4-1 for both the upper and lower leg of hysteresis. The drop in yield stress after shearing indicates the instability of agglomerates. Irreversible rupture of agglomerates by shear energy separates particles from the pair-potential energy.

Maximum yield stress occurs at 1% polymer concentration. Yield stress decreases to a minimum at 1.5% polymer in solution. Yield stress increases again, at 2% and 3% polymer concentration, and this increase is attributed to methylcellulose bridging between particles.

The fourth column of Table 4-1 shows the polymer solution viscosity. The ratio of viscosity of polymer solution (in the fourth column of Table 4-1) versus the plastic viscosity η_{PL} (in the third column of Table 4-1) varies from 1.1 to 1.5. Using a value of a=7 in the extended Einstein equation(see Equation 1.2) we get a value for relative viscosity η_r of 1.53, at ϕ=.15 .

Table 4-1: Yield Stress for Latex with 15cp. Methylcellulose

[C]	τ_B	τ_B	η_{PL}	η_{PL}	η
%	dynes/cm^2		poise		solution viscosity
	upper leg	lower leg	upper leg	lower leg	
.5	29.	7.12	.0647	.072	
.75	45.1	5.2	.0606	.0788	
1.	83.6	46.8	.0786	.114	.071
1.2	75.04	5.83	.121	.135	
1.5	51.6	4.72	.159	.182	.104
2.	117.5	7.038	.194	.25	.137
3.	200.4	22.01	.516	.593	.391

Normal Force Measurement

No normal forces were seen in any of the zones. This is consistent with the hypothesis that elastic behavior in Zone 2 and Zone 1 is a product of the depletion region effect. When a relatively low molecular weight water-soluble polymer is used for thickening, the size of the force resulting from the depletion region effect is too small to produce a large elastic component of viscoelastic behavior.

Agglomerate Size

Agglomerate size measurements for latex thickened with 15 cp. methylcellulose are shown in Figure 4-5. Agglomerate size increased in Zone 1. In Zone 2 and Zone 3, agglomerate size continuously decreased. This is consistent with the explanation that the increase in viscosity, in Zone 3 are due to interparticle bridging and solution viscosity, not to close aggregation (particles in contact).

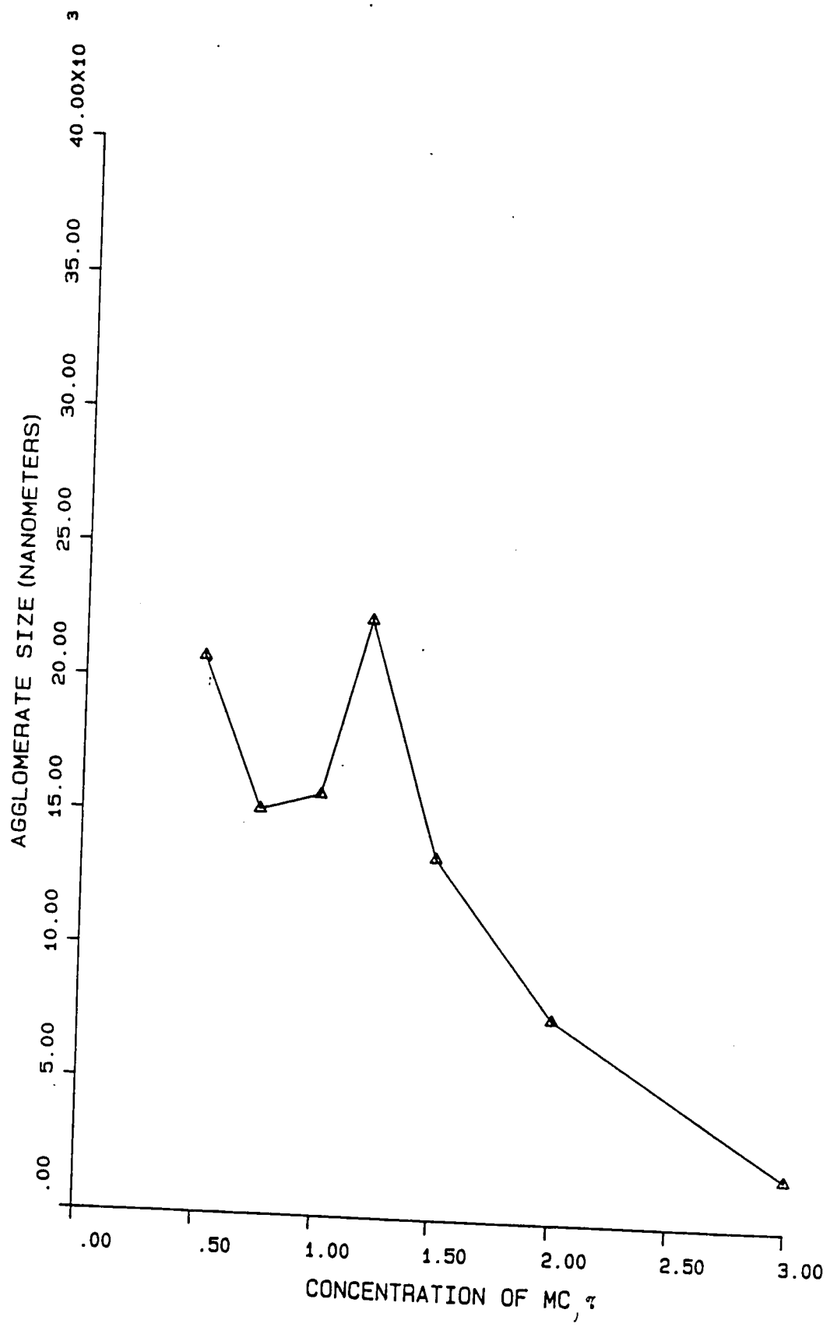

Figure 4-5: Agglomerate Size for Latex with 15 cp. Methylcellulose

4.2 400 cp. Methylcellulose

Methylcellulose having a 2% solution viscosity of 400 centipoise is known as 400 cp. methylcellulose. This polymer has a number-average molecular weight of 41,000. Thickened latex was prepared with aqueous polymer concentrations of .25%, .5%, .75%, 1.5%, 2%, and 3%. Rheology of the methylcellulose solutions at 1.5% and 2% are shown in Figure 4-6 and 4-7.

Rheology

Viscosity measurements at a shear rate of 27.88 sec^{-1} are presented in Figure 4-8. The following pages show low shear rate data. Low shear rate data are presented because high shear rate data were not available for the latex at the maximum flocculation. For the 400 cp. methylcellulose Zone 1 appears below .5%. A plot of relative viscosity versus methylcellulose concentration for the upper leg of the hysteresis curve is provided in Figure 4-9, for viscosity at a shear rate of 27.88 sec^{-1}.

Four successive points show in Figure 4-8 (at 1%, 1.5%, 2%, and 3%) the increase in viscosity of Zone 3. This increase is attributed to the effect of a higher polymer content in the continuous phase and to increased bridging associated with higher surface coverage.

An important observation is that the agglomerates in Zone 2 are very susceptible to breaking on shearing.

For all points in Zone 2, the mixing of samples led to local higher and lower concentrations initially, when the mixture was non-uniform. The local lower concentrations led to flocculation at higher agglomerate sizes than those of the final polymer concentration. In other words, because of concentration variance, the initial mixing produces oversized aggregates, which break down on

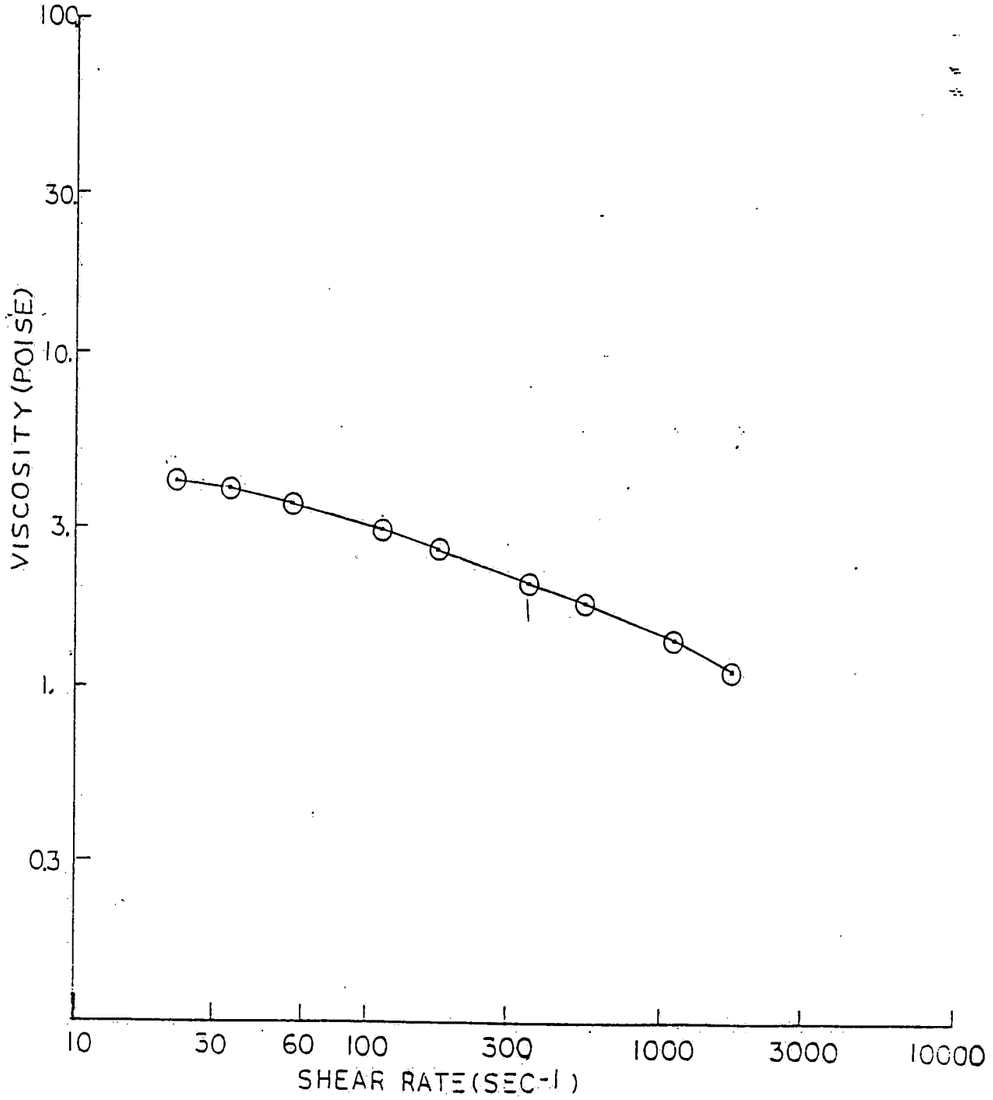

Figure 4-6: Viscosity of 1.5% 400cp. Methylcellulose

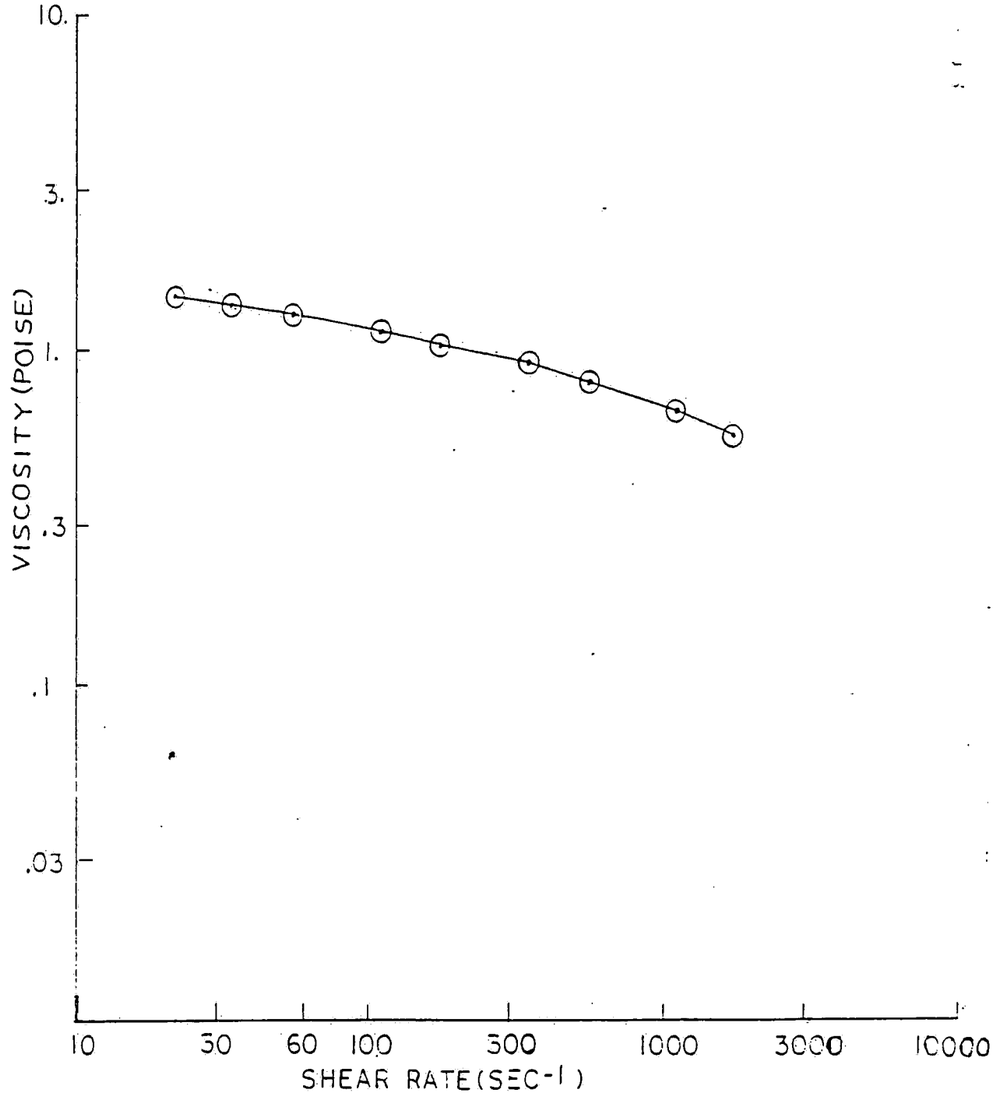

Figure 4-7: Viscosity of 2% 400 cp. Methylcellulose

shearing.

Consequently, agglomerates were formed during sample preparation which are larger than equilibrium size. This is inferred from the hysteresis results. Viscosity is reduced by reducing agglomerates to equilibrium size. The model for size equilibrium referred to is described in section 2.3.

The largest rheological hysteresis occurs throughout Zone 2 (between the viscosity maximum and viscosity minimum). The measurements in Zone 3 show a rapidly disappearing viscosity hysteresis, and the hysteresis decreases with a higher methylcellulose concentration. This means that the difference in viscosities for the increasing shear and decrease in shear leg is becoming smaller as concentration increases in Zone 3. A plot of shear hysteresis is shown in Figure 4-10, for the 1% methylcellulose concentration. In Figures 4-10 to 4-13 , the shear hysteresis is presented for higher methylcellulose polymer concentrations. Hysteresis for the 400 cp. methylcellulose-thickened latex is also shown in Figure 4-8.

Yield Stress

Yield stress data was unavailable for thickened latex with 400 cp. methylcellulose. Shear rates used for testing remained below 175 sec^{-1}. Below shear rates of 175 sec^{-1}, yield stress calculations cannot be accurately made by extrapolation.

Normal Force Measurement

Normal force measurements at a shear rate of 27.88 sec^{-1} are shown in Figure 4-14. The peak of normal force is observed at the depletion flocculation maximum. In Zone 1 , a high value for normal force is observed. Large normal forces indicate that the elastic component of thickened latex rheology increases

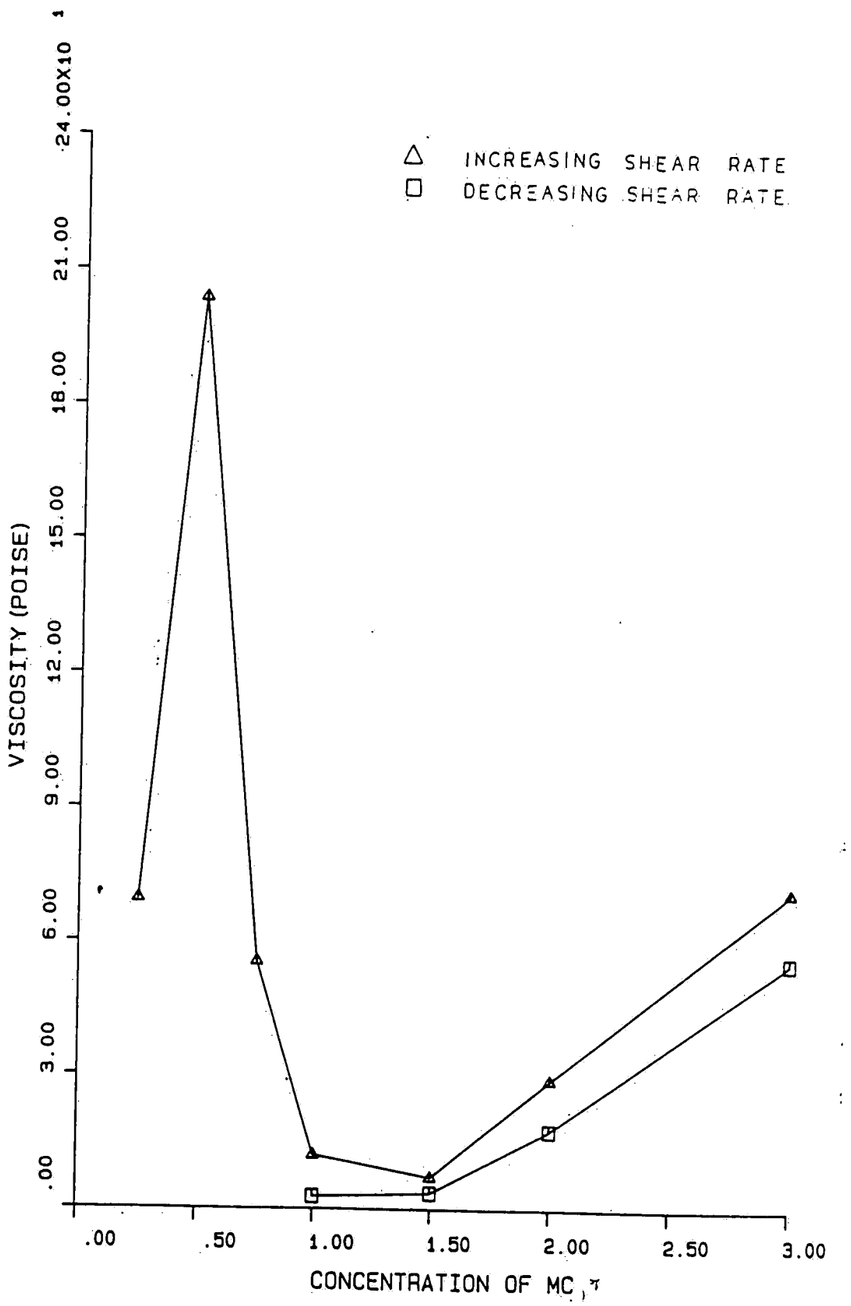

Figure 4-8: Rheology and Hysteresis for Latex with 400 cp. Methylcellulose

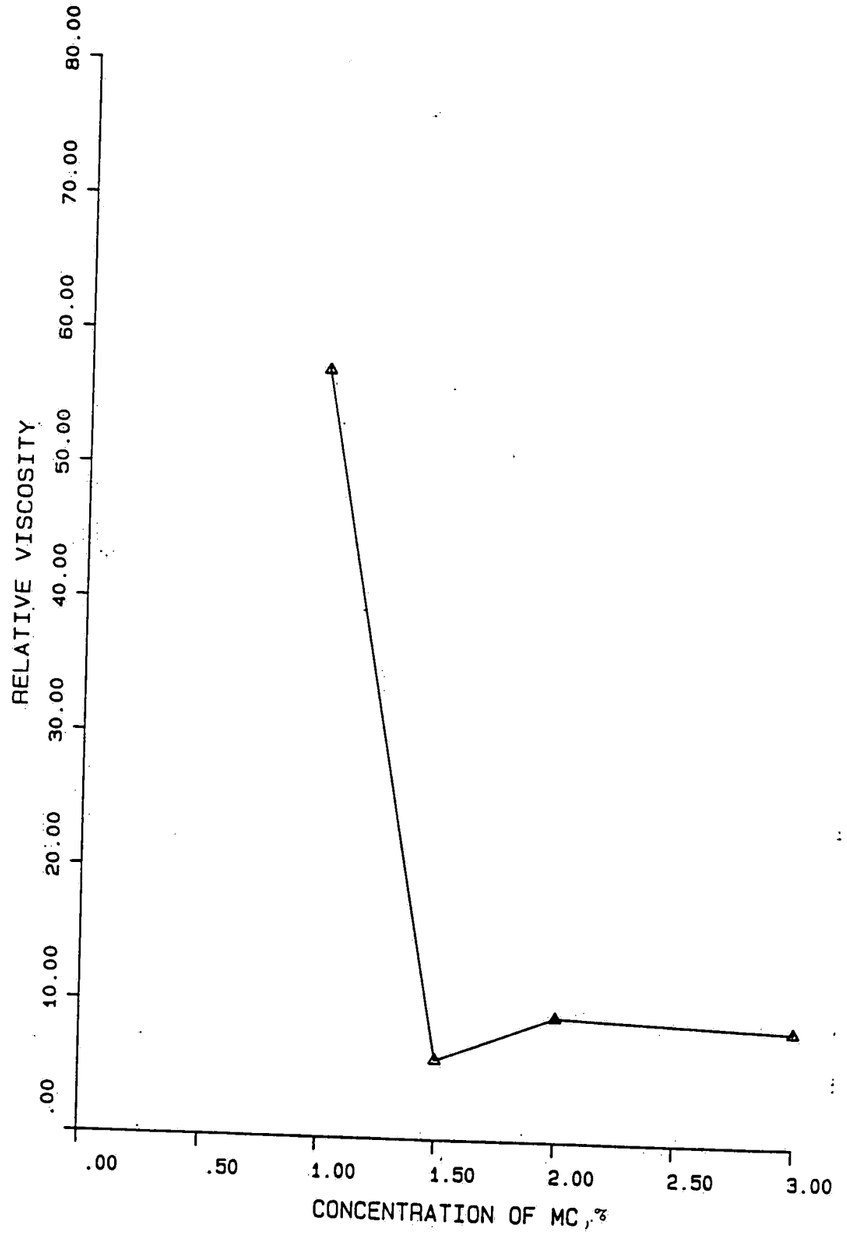

Figure 4-9: Relative Viscosity of Latex with 400 cp. Methylcellulose

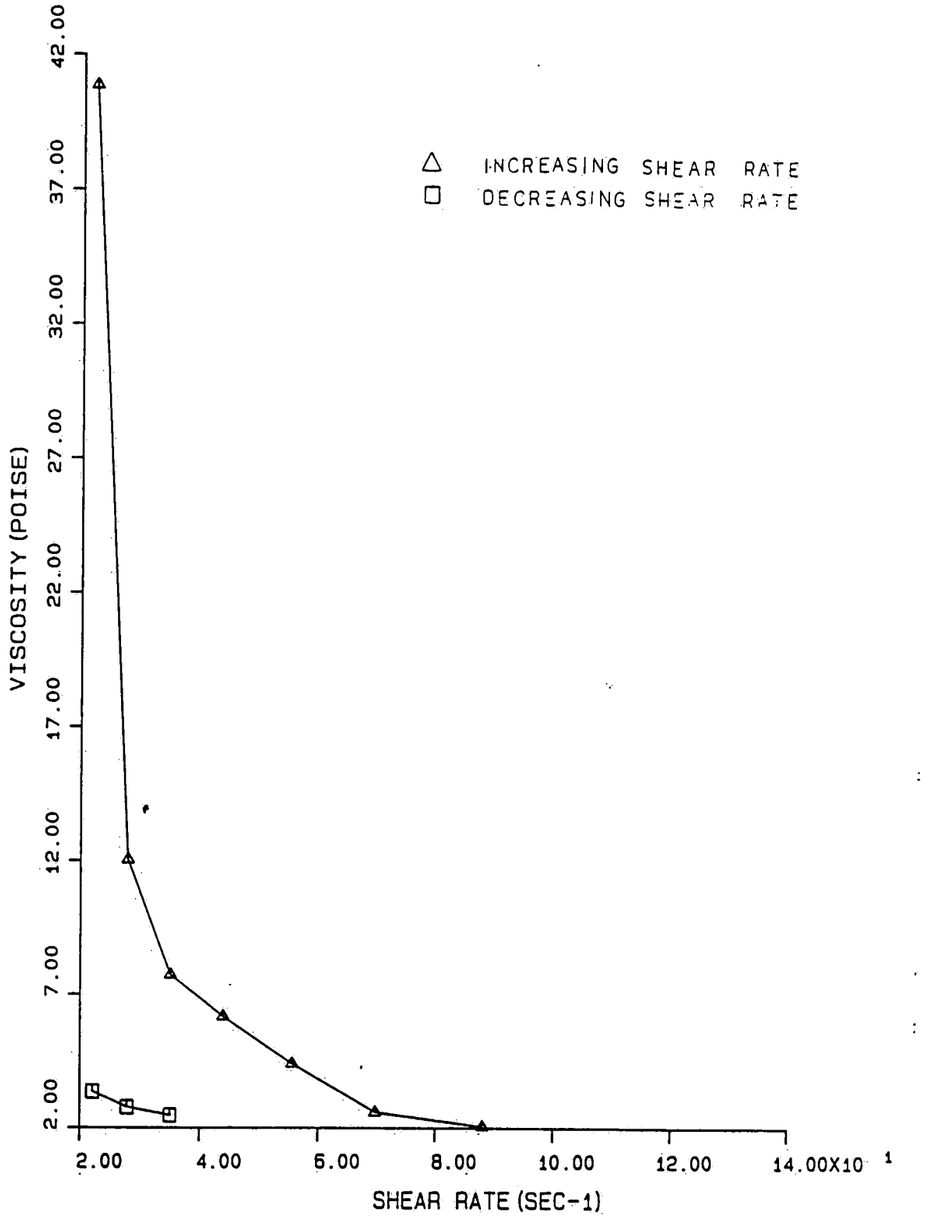

Figure 4-10: Viscosity Hysteresis for Latex with 1% 400 cp. Methylcellulose

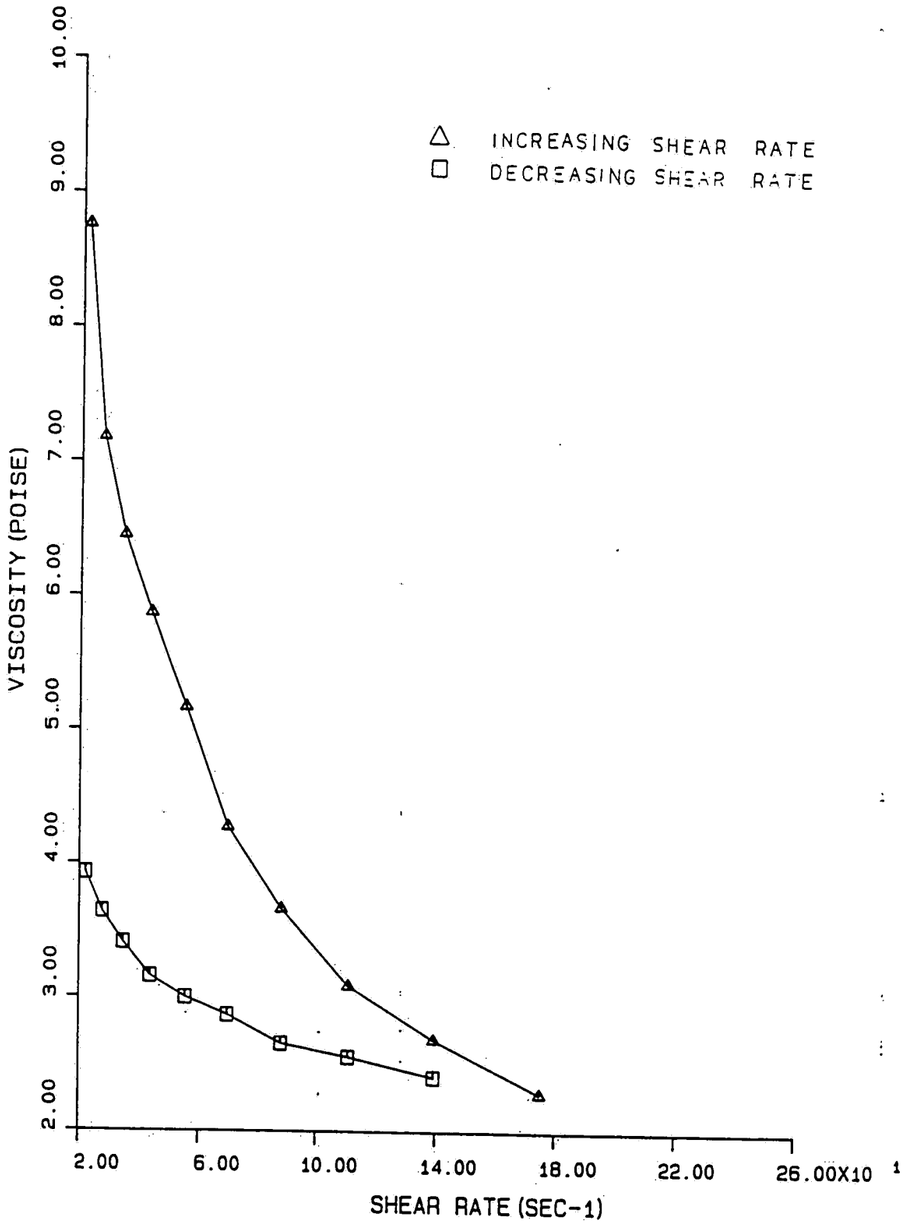

Figure 4-11: Viscosity Hysteresis for Latex with 1.5% 400cp. Methylcellulose

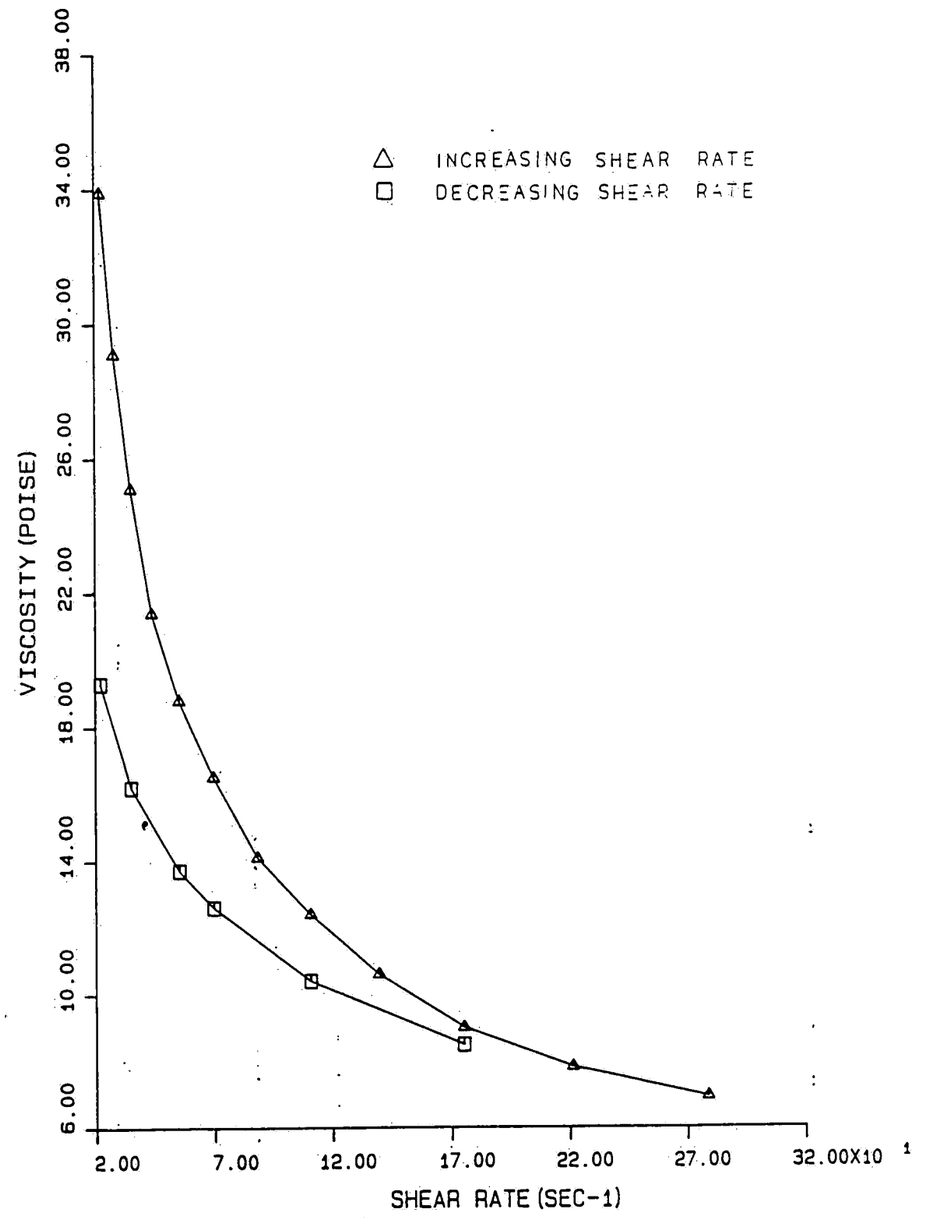

Figure 4-12: Viscosity Hysteresis for Latex with 2% 400 cp. Methylcellulose

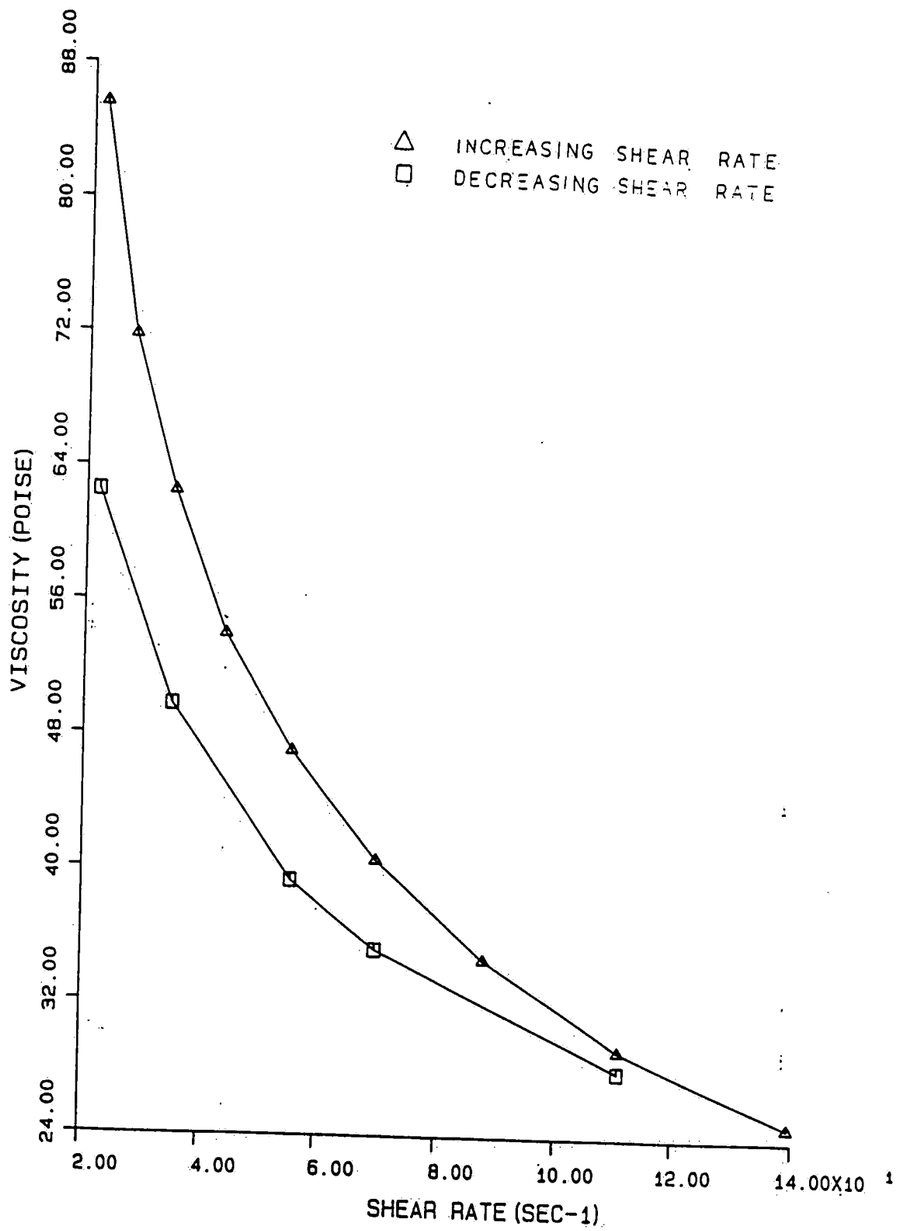

Figure 4-13: Viscosity Hysteresis for Latex with 3% 400 cp. Methylcellulose

at the concentrations where depletion flocculation takes place. For Zone 2, normal force decreases. The elastic component of rheological behavior decreases as depletion stabilization increases. In Zone 3, no normal forces are observed, which is consistent with stabilized latex and slightly increased bridging in Zone 3.

Agglomerate Size

Agglomerate size measurements for latex with 400 cp. methylcellulose are shown in Figure 4-15. The agglomerate size measured by the N-4 Nanosizer confirms that the main effect of Zone 2 is lowering the agglomerate size by the depletion stabilization effect.

Agglomerates contribute to the viscosity by dissipating energy of shearing when they are broken by shear stress and then reformed. Those agglomerates are reduced permanently in size by shearing if size is larger than equilibrium size. The permanent reduction in agglomerate size by shearing reduces the thickened latex viscosity (viscosity hysteresis).

For samples in Zone 2 on upper leg of the viscosity hysteresis curve viscosity decreases while being sheared. When shear rate is lowered after 10-15 seconds of shearing at a higher rate, then viscosity is observed to be stable while being sheared. This phenomena suggests there is a distribution of bonding energies between particles in agglomerates, requiring a specific power input for breaking each particle bonding energy, and that larger agglomerates have lower bonding energies. The pair-potential energy well is more shallow for larger radii because the annular area with $\Delta\Pi > 0$ is larger(see section 2.4). Bonding energies are the energy barriers between the metastable agglomerate size and the equilibrium agglomerate size.

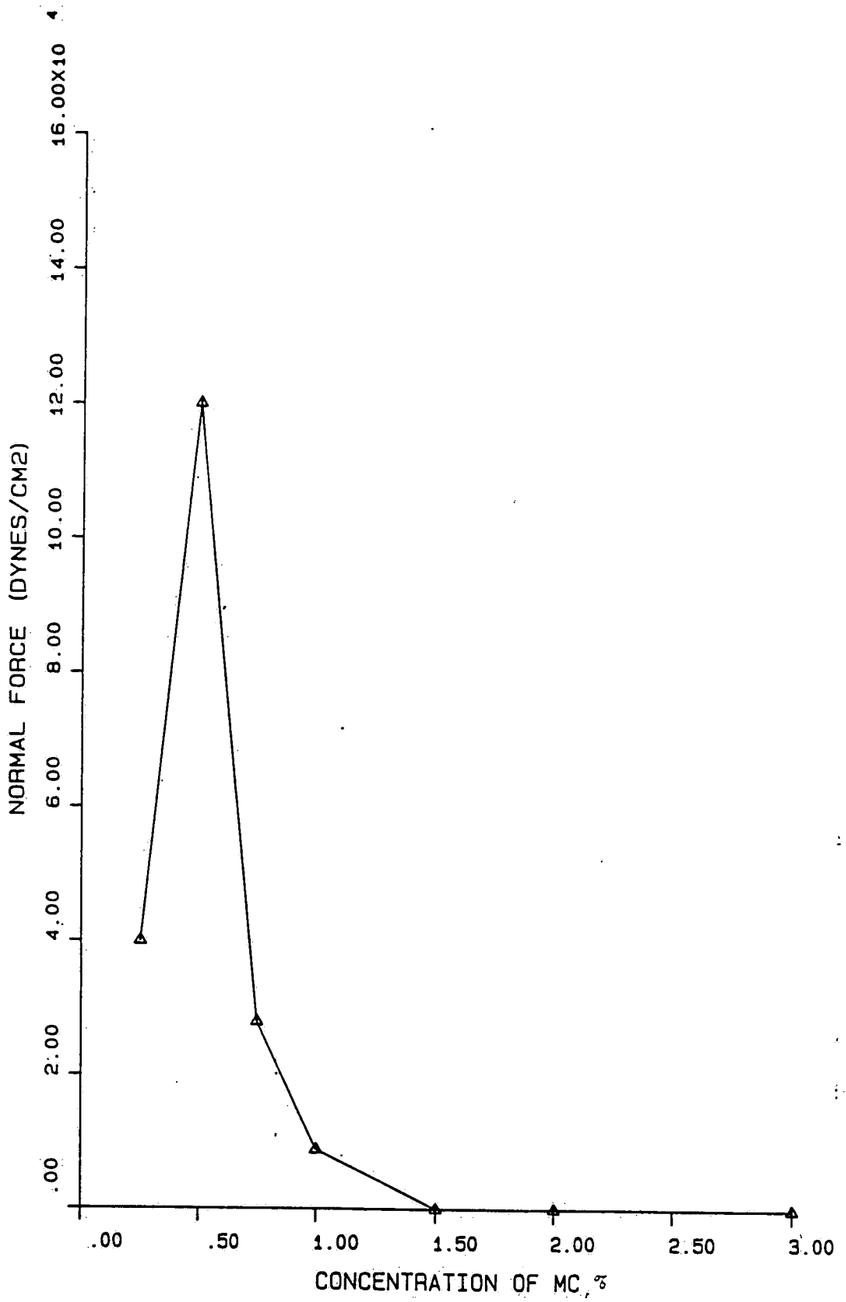

Figure 4-14: Normal Forces for Latex with 400 cp. Methylcellulose

Particles are broken when energy of shearing puts a tensile stress on the particle. If the tensile stress(correlated to the rate of energy input by shearing) is large enough, the energy well, which is the energy barrier for deflocculation, can be overcome. At each high rate of energy input, a smaller agglomerate size is approached. Energy input is equivalent to viscosity times the square of the shear rate [13].

When the energy input is reduced after shearing at a high shear rate, no aggregates are left susceptible to breaking at lower shear rate and lower energy input. We observe a stable viscosity and agglomerate size with shearing at the lower shear rates. The energy input is too small to break the remaining agglomerates.

4.3 4000 cp. Methylcellulose

The highest molecular weight methylcellulose, at 2% weight fraction in water, has a viscosity is 4000 centipoise. The molecular weight number average is 86,000. The polymer aqueous concentrations used in the thickened latex were .25%, .5%, .75%, 1%, 1.25%, 1.5%, 2%, and 2.5%.

Rheology

Viscosity measurements made at a shear rate of 22.12 sec^{-1} are shown in Figure 4-16. Low shear rate data is shown because only low shear rate viscosities are available for phase-separated samples. Figure 4-17 is a graph of relative viscosity versus polymer concentration at a shear rate of 22.12 sec^{-1}.

The lower concentrations of methylcellulose made possible the observation of both Zone 1 and Zone 2. The depletion flocculation viscosity maximum occurs between .25% and .75% methylcellulose aqueous concentration . Depletion stabilization occurs between 1.5% and 2% methylcellulose.

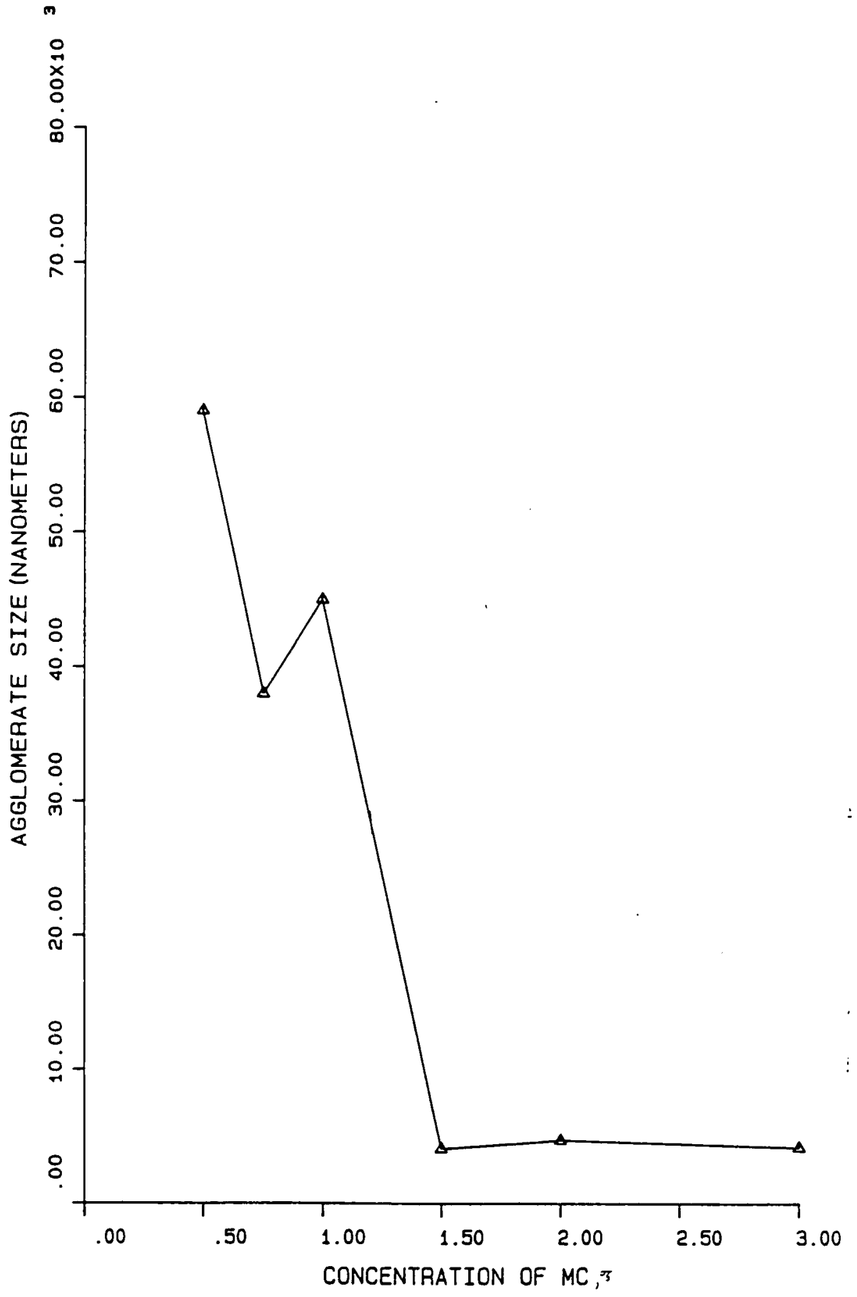

Figure 4-15: Agglomerate Sizes for Latex with 400cp. Methylcellulose

In the samples at .5% and .75% the flocculation seems to result in phase separation. Phase separation means that the latex caogualtes, the sera becomes clear, and then the sera separates from coagulated latex. This phase separation can occur on standing, and can also occur on shearing or compression of the sample.

Viscosity hysteresis for the 1% methylcellulose sample is shown in Figure 4-18.

Yield Stress

Yield stress data is not available for latex thickened with 4000 cp. methylcellulose. Shear rates used for testing remained below 175 sec^{-1}, but below shear rates of 175 sec^{-1} yield stress calculations cannot be made accurately by extrapolation.

Normal Force Measurement

Normal force measurements made at a shear rate of 11.08 sec^{-1} are shown in Figure 4-19. Data is plotted only for this low shear rate because normal force reduces with shearing, and so the actual value is time-dependent and history dependent. Given this dependence, which could not be quantified, I thought it best just to give the initial values for normal force. The measurement of normal force shows that elasticity increases in Zone 1 , and decreases in Zone 2. Except for the point at 1.25% concentration of methylcellulose, a regular decrease in elasticity occurs in Zone 2.

Agglomerate Size Measurement

Agglomerate size measurements were made at all concentrations of polymer, and are shown in Figure 4-20. Latex with .25% polymer in solution was unstable, giving no constant or reproducible results. At .5% and .75%,

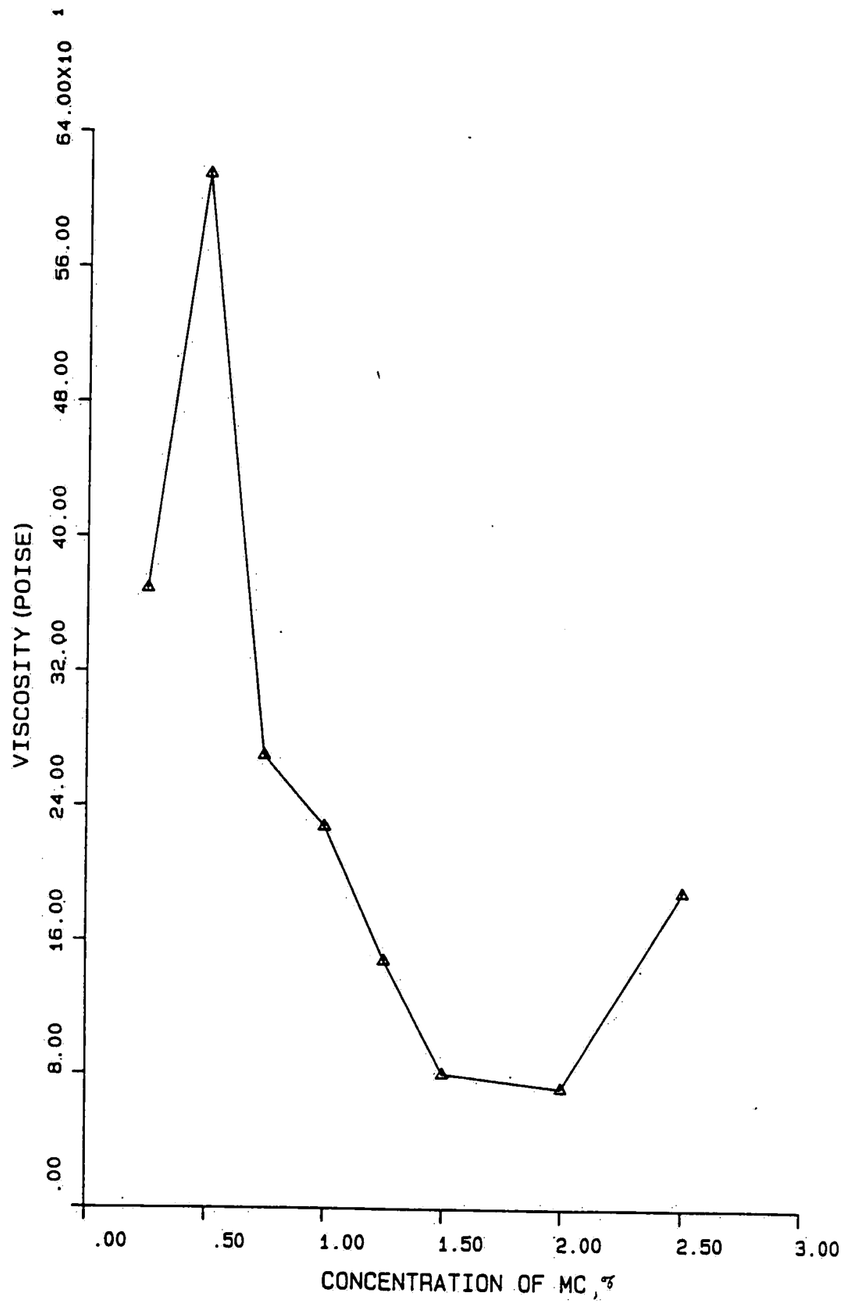

Figure 4-16: Rheology of Latex with 4000 cp. Methylcellulose

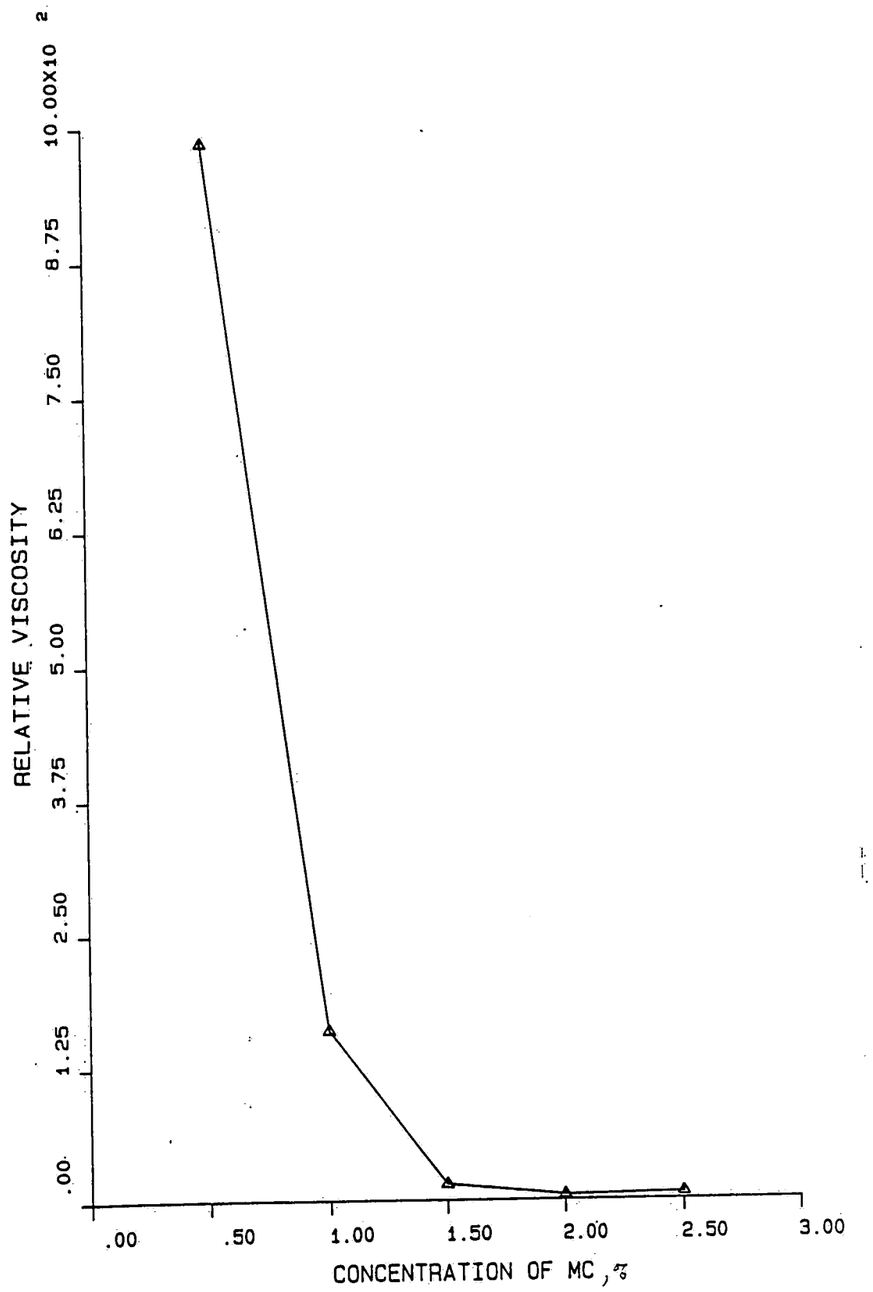

Figure 4-17: Relative Viscosity of Latex with 4000 cp. Methylcellulose

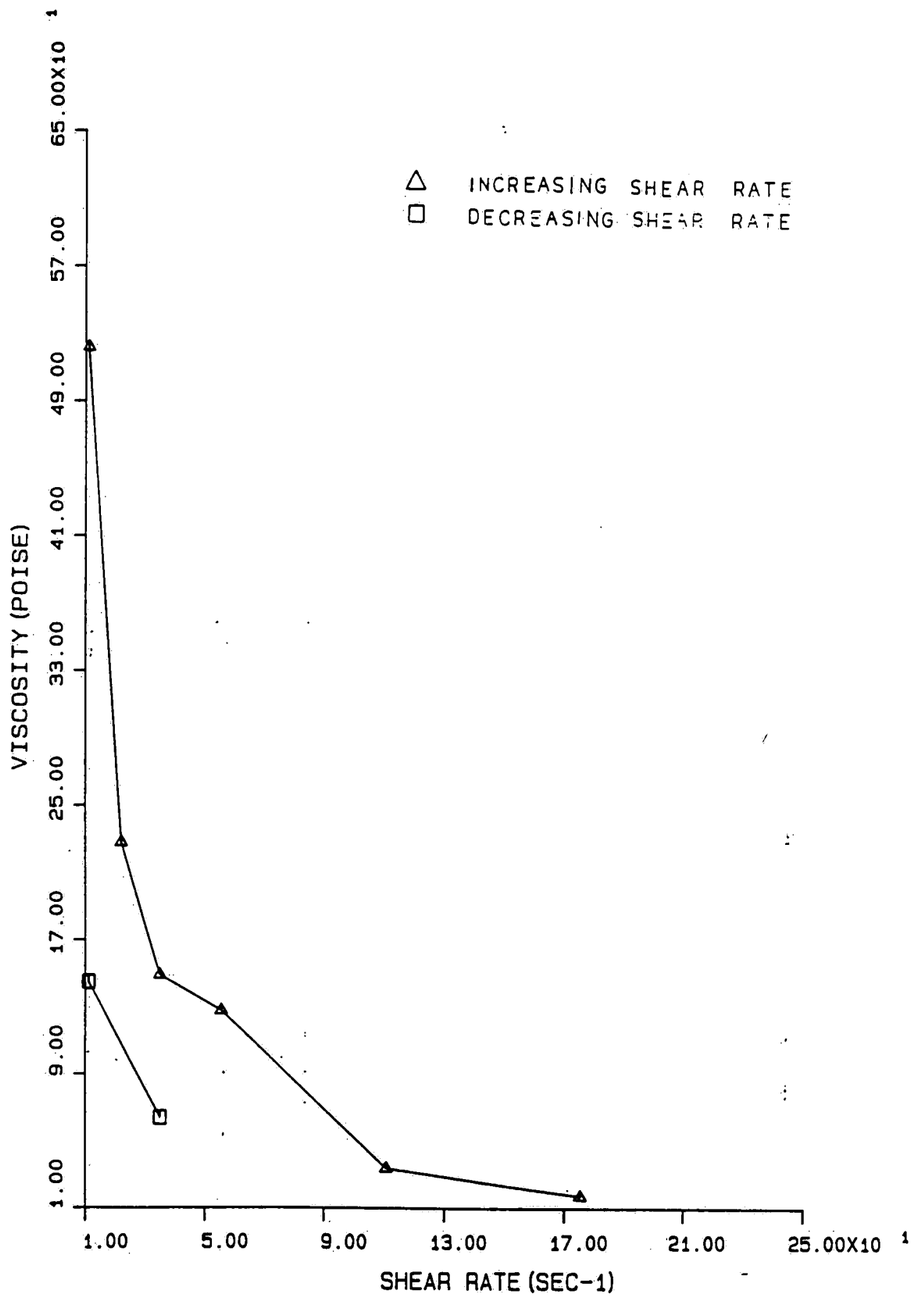

Figure 4-18: Viscosity Hysteresis for Latex with 1% 4000 cp. Methylcellulose

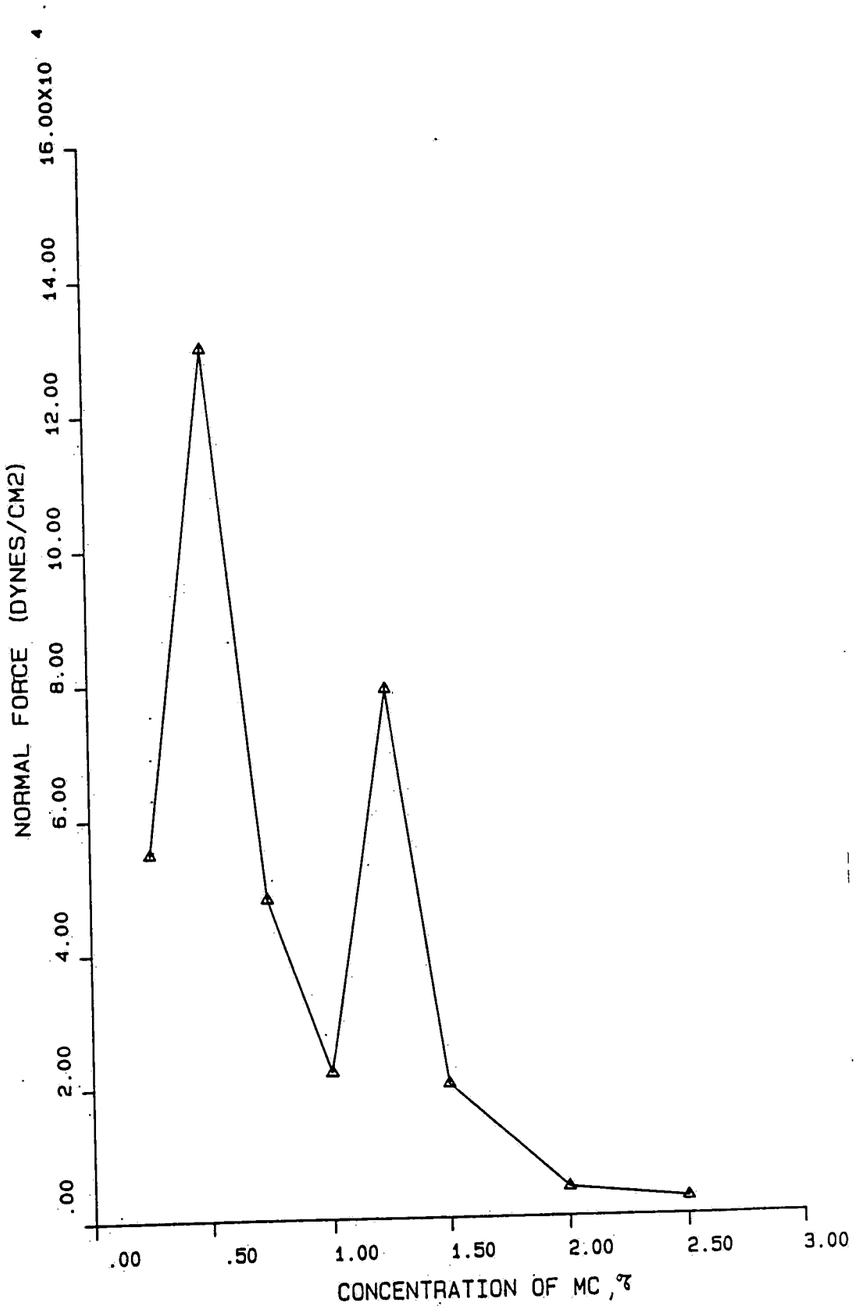

Figure 4-19: Normal Forces for Latex with 4000cp. Methylcellulose

since phase separation took place, the agglomerate sizes were macroscopic, and quickly settled on dilution. When the agglomerates settle to the bottom of the sample chamber, they do not scatter light. The particles scattering light are from the clear sera after phase separation. The diameters measured gave only the initial particle size, or slightly larger(200-400 nm.).

The samples containing 1%, 1.25%, and 1.5% methylcellulose polymer in solution, had a lower viscosity . These samples had agglomerates in a measurable size range (20-25 microns). In this particle size range the Nanosizer has very limited accuracy .

4.4 Comparative Results for Methylcellulose Thickened Latex

By comparing results from all three molecular weights , the effect of molecular weight on aggregation can be determined.

One important observation is that a change in molecular weight has a very strong effect on viscosity. The position of the depletion maximum(Zone 1-Zone 2 boundary) is shifted to lower polymer concentration when viscosity average molecular weight increases from 15,000 to 41,000 .The polymer concentration at the depletion maximum shifts from 1.2% to .5%.

Viscosity at the depletion flocculation maximum increases strongly with molecular weight. For 15 cp. methylcellulose (MW=15,000) the viscosity at maximum depletion flocculation (at 1.2% methylcellulose concentration) is 2.04 poise. For 400 cp. methylcellulose (MW=41,000) the viscosity at maximum depletion flocculation (at .5% methylcellulose concentration) is 204 poise. For 4000 cp. methylcellulose (MW=86,000) the viscosity at maximum depletion flocculation is 615 poise.

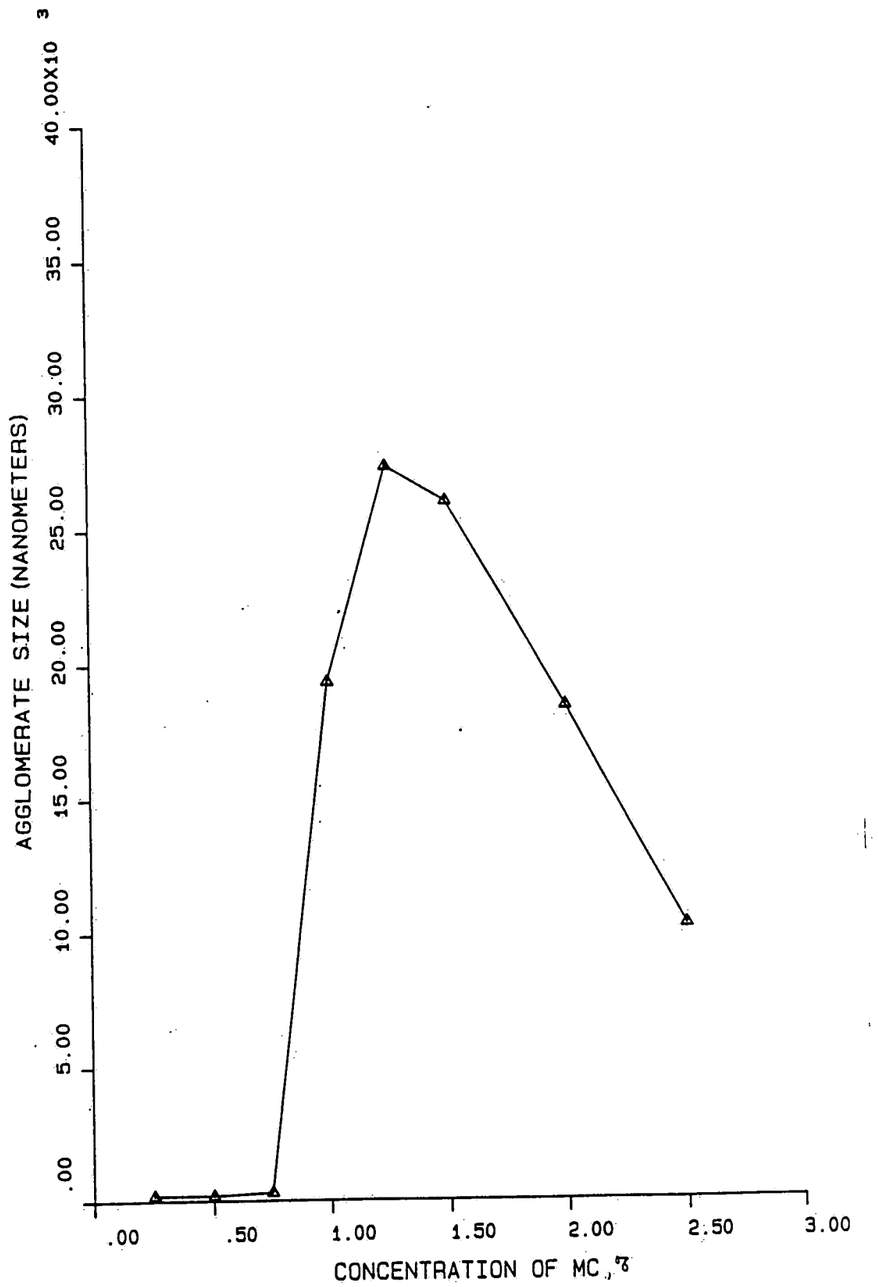

Figure 4-20: Agglomerate Size for Latex with 4000 cp. Methylcellulose

Chapter 5
Conclusions

The primary conclusion from this work is that methylcellulose coagulates cleaned polystyrene latex by a depletion flocculation or exclusion volume effect. The cleaned latex is both emulsifier-free and salt-free. For polymer concentrations up to the depletion flocculation maximum, the viscosity and agglomerate sizes increase. This polymer concentration region is called Zone 1.

The critical polymer concentration at the depletion flocculation maximum decreases with increasing molecular weight. For the 4000 cp. and 400 cp. methylcelluloses, the polymer concentration at the flocculation maximum is .5%. For the 15 cp. methylcellulose, the polymer concentration at the flocculation maximum is 1.2%.

For polymer concentrations above the depletion flocculation maximum, the viscosity and agglomerate sizes decrease to the depletion stabilization minimum. This polymer concentration region is called Zone 2 .

Beyond the point of depletion stabilization, agglomerate sizes remains stable or decreases, and viscosity increases. The increase in viscosity can be attributed to bridging by polymer and to polymer solution viscosity. This polymer concentration region is called Zone 3.

The concentrations near the depletion flocculation maximum may have a set of concentrations where phase separation occurs. The size of this region depends on the polymer molecular weight. Phase separation was only observed for the highest molecular weight methylcellulose(MW_n=86,000).

The free energy change for depletion flocculation is dependent on the molecular weight of the polymer used. The higher the molecular weight, the

larger the free energy change for flocculation. The large energy required for separation of particles results in the viscosity maximum for depletion flocculation.

Stabilization is larger for a higher molecular weight . The viscosity difference between viscosity at depletion flocculation and viscosity at depletion stabilization increases with increasing molecular weight. For the 15 cp. methylcellulose, this difference is 1.05 poise. For 400 cp. methylcellulose, this difference is 195.2 poise. For 4000 cp. methylcellulose, this difference is 542.5 poise.

Mixing produces agglomerates larger than equilibrium. On shearing, these agglomerates reduce towards an equilibrium size. This reduction in agglomerate size results in viscosity hysteresis. The viscosity hysteresis shows that aggregates can be broken permanently by shearing if they are larger than the equilibrium size. Agglomerate size correlated well with viscosity. Larger agglomerates result in higher viscosities because energy of shearing is dissipated by agglomerates which break and reform. The forces which hold agglomerates together depend on polymer molecular weight and concentration.

Chapter 5
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